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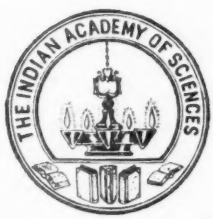

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DYES DERIVED FROM CHRYSOQUINONE.

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and
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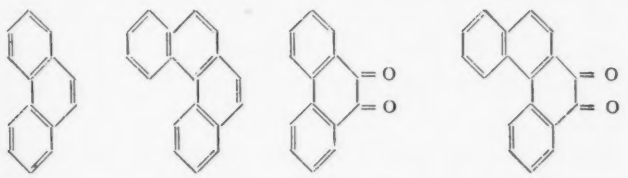
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Until before the War, the hydrocarbon phenanthrene which is present in anthracene oil or green oil to the extent of about 30 per cent., and which is so interesting from the theoretical point of view, was almost a waste product and was scarcely manufactured in the pure state. In 1916, Mukherjee and Watson[1] prepared an interesting series of vat and other dyestuffs from phenanthraquinone. The work was continued by Watson and Dutt,[2] Sircar and Dutt[3] and Dutt,[4] and phenanthraquinone was shown to be capable of yielding quite an interesting array of colouring matters of great technical value, and some of these are actually being manufactured.

Chrysene or naphthphenanthrene is another hydrocarbon of coal tar obtained from the higher boiling fractions, which has not found any technical application as yet, and as such, it has still remained of purely theoretical interest. Structurally, the two hydrocarbons phenanthrene (I) and chrysene (II) and their oxidation products, phenanthraquinone (III) and chrysoquinone (IV) are so closely alike, that it is quite natural to expect that chrysene



(I) (II) (III) (IV)

would yield dyestuffs closely analogous to phenanthrene. This was supported by the observations of the present authors that chrysoquinone dyes wool and cotton from an alkaline hydrosulphite vat to beautiful orange shades. The present investigation was therefore undertaken with the object of preparing colouring matters from chrysene *via* chrysoquinone. The attempts were divided into three parts :

A. Attempts to Prepare New Hydroxy Derivatives.

It has been shown by Mukherjee and Watson[1] that the introduction of hydroxy groups into the molecule of phenanthraquinone even by methods of great value in the case of anthraquinone dyestuffs, namely by the action of fuming sulphuric acid and boron trioxide and also by concentrated sulphuric acid and manganese dioxide, was impossible on account of the ease with which the molecule was destroyed by oxidation by these reagents. Similar difficulties were met with in the case of chrysoquinone, and therefore, it was thought advisable to prepare the hydroxy derivatives through nitration, reduction and subsequent diazotisation followed by hydrolysis.

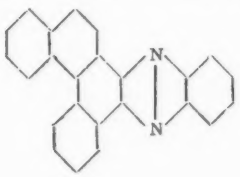
The nitration was successful, but the amines could not be obtained in any yield by reduction, as during the process of reduction with a metal and acid, the amines formed metallic complexes which were quite insoluble in water and consequently could not be satisfactorily decomposed with hydrogen sulphide.

B. Attempts to Prepare Anilino Derivatives of Chrysoquinone.

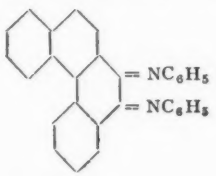
On account of serious difficulties in the methods to produce amino-derivatives from chrysoquinone, the possibilities of dyes in the form of hydroxy-chrysoquinones or acylamino-chrysoquinones were out of question. Consequently the bromination of chrysoquinone with formation of mono- and polybromo derivatives was the only practicable first step towards the production of anilino-chrysoquinones. It was possible to prepare three bromo derivatives of chrysoquinone, two of which were isomeric monobromo derivatives and the third was a pentabromo derivative. From these three bromo derivatives, three anilino derivatives were subsequently obtained, two of which were isomeric monoanilino derivatives and the third was a tetraanilino-monobromo derivative. These have got interesting dyeing properties and dye wool in violet shades.

C. Attempts to Prepare Condensation Products of Chrysoquinone with Aromatic Amines.

Chrysoquinone condenses fairly easily with aromatic amines with formation of chrysophenazines (V) and chrysoquinone-anilides (VI) and condensation



(V)



(VI)

products were obtained with the following amines : *o*-phenylene-diamine, *o*-aminophenol, 1 : 2-naphthalenediamine, *o*-anisidine, *o*-toluidine, *m*-toluidine, α-naphthylamine, β-naphthylamine, *o*-phenetidine, *p*-phenetidine, aniline, phenylhydrazine and 2 : 3-diamino-phenazine. The behaviour of all the azines and anilides obtained in this way was normal. All these compounds on examination were found to be good dyestuffs. They dye unmordanted wool from an acid-bath, and also cotton from hydrosulphite vat in various shades ranging from brilliant yellow to dark violet. Their absorption maxima range from 4,400 to 5,900 in Angstrom units.

Experimental.

Preparation of chrysoquinone.—The best oxidising agent for the preparation of chrysoquinone was found to be sodium dichromate in glacial acetic acid. Finely powdered chrysene (5 gm.) was added to a solution of sodium dichromate (22 gm.) in glacial acetic acid (50 c.c.) and the mixture refluxed on a sand-bath for nine hours. An equal volume of hot water was then added and the crystalline precipitate of chrysoquinone filtered off and recrystallised from boiling glacial acetic acid. Orange-red glistening plates, melting at 239° C. Yield, 4·75 gm.

Mononitro-chrysoquinone.—Chrysoquinone (1 gm.) was dissolved in concentrated nitric acid (S.G. 1·4, 10 c.c.) and the solution allowed to stand for 24 hours. The mixture on dilution with water yielded the nitro-derivative as a yellow precipitate, which was crystallised from nitrobenzene in glistening yellow needles, melting at 256–57° C. (Found : N = 4·85 ; $C_{18}H_9O_4N$ requires N = 4·62 per cent.)

Dinitro-chrysoquinone.—Chrysoquinone (1 gm.) was heated with concentrated nitric acid (10 c.c.) on a water-bath under reflux for three hours. On cooling the solution, the dinitro derivative separated out in orange-yellow crystals. The product was recrystallised from nitrobenzene in fine yellow prisms melting at 235° C. Yield, 0·75 gm. (Found : N = 8·81 ; $C_{18}H_8O_6N_2$ requires N = 8·59 per cent.)

Tetranitro-chrysoquinone.—Chrysoquinone (1 gm.) was treated with fuming nitric acid (S.G. 1·51, 10 c.c.) and the resultant solution heated on the water-bath under reflux for eight hours. On cooling the tetranitro derivative separated as an orange microcrystalline powder. The substance is insoluble in all the organic solvents. It can only be recrystallised from fumimg nitric acid in microscopic prisms, melting above 300° C. Yield, 1·21 gm. (Found : N = 12·5 ; $C_{18}H_6O_{10}N_4$ requires N = 12·78 per cent.)

Monobromo-chrysoquinone (*A*)—Chrysoquinone was dissolved in nitrobenzene (1 gm. in 20 c.c.) and the solution treated with bromine (1 c.c.) in

the same solvent (10 c.c.). The mixture was heated on an oil-bath under reflux at 110° C. for two hours. On cooling the monobromo compound crystallised out in yellow glistening leaflets melting at 246° C. (Found : Br = 24·1 ; $C_{18}H_9BrO_2$ requires Br = 23·7 per cent.)

Monobromo-chrysoquinone (*B*).—This substance was prepared in the same manner as the above-mentioned compound with the exception that glacial acetic acid was used as the solvent instead of nitrobenzene. The substance crystallised from glacial acetic acid in glistening yellow needles melting at 218° C. (Found : Br = 24·08 ; $C_{18}H_9BrO_2$ requires Br = 23·7 per cent.)

Pentabromo-chrysoquinone.—Chrysoquinone (1 gm.) was heated with a large excess of bromine (5 c.c.) in a sealed tube under pressure at 100° C. for six hours. The product was crystallised from nitrobenzene in glistening orange-yellow leaflets melting above 300° C. (Found : Br = 64·8 ; $C_{18}H_5Br_5O_2$ requires Br = 64·3 per cent.)

Monoanilino-chrysoquinone (*A*).—This was obtained from monobromo-chrysoquinone (A) by treatment with aniline in presence of copper-bronze according to the well-known method of Ullmann. The anilino compound was crystallised from a mixture of nitrobenzene (1 part) and glacial acetic acid in dark brown microscopic needles melting at 210–12° C. (Found : N = 4·17 ; $C_{24}H_{15}O_2N$ requires N = 4·01 per cent.)

Monoanilino-chrysoquinone (*B*).—This was prepared from monobromo-chrysoquinone (B) in the same way as the above-mentioned compound. It could not be crystallised, but was purified from alcohol. The substance is a dark green powder melting at 153–55° C. (Found : N = 4·47 ; $C_{18}H_{15}O_2N$ requires N = 4·01 per cent.)

Tetranilino-bromo-chrysoquinone.—This was obtained from pentabromo-chrysoquinone by Ullmann's reaction with aniline in the usual manner. It could not be crystallised, but was purified by solution in nitrobenzene and precipitation with alcohol. It is a dark brown powder melting at 291–93° C. (Found : N = 47 ; $C_{42}H_{29}O_2N_4Br$ requires N = 7·98 per cent.)

Chrysophenazine.—This was obtained by condensation of chrysoquinone with *o*-phenylene diamine in molecular proportions in boiling glacial acetic acid solution. It crystallised from nitrobenzene in glistening yellow needles melting at 207–08° C. and from glacial acetic acid in bright yellow prisms melting at 199° C. (Found : N = 8·08 ; $C_{24}H_{14}N_2$ requires N = 8·48 per cent.)

Chryso-1 : 2-*naphthazine*.—This was obtained in a similar way to the above, by using 1 : 2-naphthalene-diamine in place of *o*-phenylenediamine.

It crystallised from boiling toluene in bright yellow needles with a silky lustre. M.P. 238° C. (Found : N = 7·23 ; $C_{28}H_{16}N_2$ requires N = 7·36 per cent.)

Chrysophenoxozine.—This was obtained by condensation of chrysoquinone (1 mol.) with *o*-aminophenol (2 mols.) in hot glacial acetic acid solution. The dark brown precipitate obtained by pouring the reaction product into water was crystallised from alcohol in brown microscopic needles melting at 236° C. (Found : N = 6·5 ; $C_{30}H_{20}O_2N_2$ requires N = 6·8 per cent.)

Chrysoquinone-di-anilide.—This was obtained by the condensation of chrysoquinone with excess of aniline in glacial acetic acid solution. The reaction product was poured into dilute hydrochloric acid and the precipitated compound crystallised from a mixture of equal parts of nitrobenzene and alcohol in dark brown microscopic needles melting at 228–29° C. (Found : N = 6·42 ; $C_{30}H_{20}N_2$ requires N = 6·86 per cent.)

*Chrysoquinone-di-*o*-toluidide.*—This was obtained from chrysoquinone and *o*-toluidine in a similar way to the above. Brown needles melting above 300° C. (Found : N = 6·6 ; $C_{32}H_{24}N_2$ requires N = 6·4 per cent.)

*Chrysoquinone-di-*m*-toluidide.*—Obtained from chrysoquinone and *m*-toluidine as above. Brown needles melting at 163–65° C. (Found : N = 6·24 ; $C_{32}H_{24}N_2$ requires N = 6·4 per cent.)

*Chrysoquinone-di-*o*-anisidide.*—This was obtained by condensing chrysoquinone with excess of *o*-anisidine in boiling glacial acetic acid solution. After refluxing for three hours, the product was poured into dilute hydrochloric acid, and the precipitate crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown needles. M.P. 160–63° C. (Found : N = 5·92 ; $C_{32}H_{24}N_2O_2$ requires N = 5·65 per cent.)

*Chrysoquinone-di-*o*-phenetidide.*—Chrysoquinone (2 gm.) was directly condensed with *o*-phenetidine (5 gm.) by heating under reflux for three hours. The product was poured into dilute hydrochloric acid and the precipitated compound crystallised from alcohol. M.P. 188–90° C. (Found : N = 5·44 ; $C_{34}H_{28}O_2N_2$ requires N = 5·6 per cent.)

*Chrysoquinone-di-*p*-phenetidide.*—This was obtained from chrysoquinone and *p*-phenetidide in the same way as above. M.P. 205–07° C. (Found : N = 5·56 ; $C_{34}H_{28}O_2N_2$ requires N = 5·6 per cent.)

Chrysoquinone-di-α-naphthylimide.—This was obtained from chrysoquinone and α-naphthylamine by condensation in hot glacial acetic acid solution, in the usual manner. The product crystallised from a mixture of equal volumes of nitrobenzene and glacial acetic acid in dark brown

needles melting at 198–200° C. (Found : N = 5·32 ; $C_{38}H_{24}N_2$ requires N = 5·47 per cent.)

Chrysoquinone-di-β-naphthylimide.—This was obtained from chrysoquinone and β-naphthylamine in the same way as the above. M.P. 203° C. (Found : N = 5·83 ; $C_{38}H_{24}N_2$ requires N = 5·47 per cent.)

Properties of the Chrysoquinone Dyestuffs.

Name of the compound (c.q. = chrysoquinone)	Shade of dyeing on wool from acid-bath	Shade of dyeing on cotton from hydrosulphite vat	Absorption maxima in wave-lengths
Chrysoquinone	Light yellow	Orange yellow	4400
Mononitro-c.q.	..	Light orange	4400
Dinitro-c.q.	..	Light brown	4560
Tetranitro-c.q.	..	Light brown	Insoluble
Monobromo-c.q. (A)	..	Light yellow	4350
Monobromo-c.q. (B)	..	Light yellow	4400
Monoanilino-c.q. (A)	Dark neutral grey	Dark grey	5850
Monoanilino-c.q. (B)	Dark reddish-violet	Brownish-violet	5900
Tetranilinobromo-c.q.	..	Bottle green	Insoluble
Chrysophenazine	Greenish-yellow	Greenish-yellow	4350
Chrysonaphthazine	Greenish-yellow	Greenish-yellow	4350
Chrysophenoxazine	Orange-yellow	Orange-yellow	4350
C.q.-dianilide	Medium yellow	..	4850
C.q.-di-*o*-toluidide	Medium yellow (broken tones)	..	4970
C.q.-di-*m*-toluidide	Dark neutral-grey	..	4900
C.q.-di-anisidide	Medium grey	..	5870
C.q.-di-*o*-phenetidide	Dark neutral-grey	..	5900
C.q.-di-*p*-phenetidide	Greyish-yellow	..	Insoluble
Chryso-2 : 3-diamidophenazineazine	Dark reddish-violet	..	5050
C.q.-di-α-naphthylimide	Dark violet-red	..	5270
C.q.-di-β-naphthylimide	Light violet	..	5100
C.q.-di-phenylhydrazone	Dark brown	..	5150

Chrysoquinone-diphenylhydrazone.—This was obtained from chrysoquinone and excess of phenylhydrazine in glacial acetic acid solution, in the usual manner. It crystallised from a mixture of equal parts of nitrobenzene and glacial acetic acid in dark brown microscopic needles melting at 228–29° C. (Found : N = 12·65 ; $C_{30}H_{22}N_4$ requires N = 12·78 per cent.)

Chryso-2 : 3-*diamidophenazineazine.*—This was obtained from chrysoquinone and 2 : 3-diamidophenazine by condensation in glacial acetic acid solution. The substance was crystallised from nitrobenzene in almost black needles melting above 300° C. (Found : N = 12·8 ; $C_{30}H_{16}N_4$ requires N = 12·9 per cent.)

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1. Mukherjee and Watson, *J. Chem. Soc.*, T., 1916, **109**, 617.
2. Watson and Dutt, *ibid.*, 1921, **119**, 1211.
3. Sircar and Dutt, *ibid.*, 1922, **121**, 1944.
4. Dutt, *ibid.*, 1922, **121**, 1951.

STUDIES IN THE FRIEDEL-CRAFTS REACTION.

Part IV. The Action of Acetyl Chloride and Acetic Anhydride on Resorcinol and its Derivatives. An Evidence for γ-Substitution in the Resorcinol Nucleus.

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Received August 31, 1938.

(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

Phenolic ethers have been condensed with acetyl chloride and acetic anhydride in the presence of anhydrous aluminium chloride with the formation of methoxy-acetophenones which, on demethylation, give their hydroxy-derivatives. The literature is very scanty with regard to the use of free phenols in such condensations. As we required O-hydroxy-acetophenones and their substitutuion products for the coumarin as well as the chromone synthesis, we thought that the best method would be the application of the Friedel-Crafts Reaction to the free phenols themselves. The Nencki Reaction[1] which usually gives this type of ketones does not give a good yield when higher fatty acids or aromatic acids are used.

An additional point of interest attaches itself to the use of resorcinol and its derivatives in this type of condensation from the view-point of substitution. Resorcinol (or 1 : 3-dihydroxy-benzene) undergoes monosubstitution at position 4 (B-substitution) and not at position 2 (Y-substitution) because the former position receives a greater amount of electron-accession from the two hydroxyl groups than the latter. The second substituent takes up again position 6 (β-position) and not position 2, which is attacked only when positions 4 and 6 are occupied. Baker and co-workers[2] have brought forward some evidence of γ-substituion in the case of certain derivatives of resacetophenone, and our object has been to see whether γ-substitution would take place in the case of resorcinol or its monosubstitution derivatives. With this object in view, we have condensed resorcinol, 4-ethylresorcinol, β-methylresorcylate, resacetophenone (4-acetylresorcinol) and orcinol with either acetyl chloride or acetic anhydride with the following results :—

Resorcinol and acetyl chloride gave 4-acetyl resorcinol unaccompanied by any trace of 2-acetylresorcin. Similarly 4-ethylresorcinol yielded 2 : 4-dihydroxy-5-ethylacetophenone, not a trace of the isomeric 2 : 6-dihydroxy-3-ethylacetophenone being formed. An authentic specimen of the latter ketone

was synthesised from methyl 2 : 4-dihyrdoxy-5-ethylbenzoate and acetyl chloride in the presence of anhydrous aluminium chloride, hydrolysing the resulting ester, and decarboxylating the corresponding acid. The same ketone was also obtained from Shah and Samant's[3] 7-hydroxy-6-ethyl-4-methyl coumarin by Limaye's process.[4] Incidentally we have studied some of the properties of 8-acetyl-7-hydroxy-6-ethyl-4-methyl coumarin, *e.g.*, the preparation of functional derivatives, bromination and hydrolysis of the bromocoumarin.

β-Methylresorcylate did not condense with acetyl chloride at the ordinary temperature, but acetic anhydride at 100° gave methyl 2 : 4-dihydroxy-5-acetyl benzoate unaccompanied by any detectable trace of the isomeric methyl 2 : 4-dihydroxy-3-acetyl benzoate. The constitution of the ester was proved by following the method of Liebermann and Lindemann.[5]

Resacetophenone and acetic anhydride gave an equimolecular mixture of 2 : 4-diacetyl- and 4 : 6-diacetylresorcinols. Orcinol reacted with acetyl chloride giving mainly orsacetophenone (2 : 4-dihydroxy-6-methylacetophenone) to gather with a small amount of 5-hydroxy-4 : 7-dimethyl coumarin which could arise only from the isomeric 2 : 6-dihydroxy-4-methyl-acetophenone, by the acetylation of one of the hydroxyl groups and subsequent ring-closure.

Thus we conclude from our experiments that resacetophenone and orcinol are the only two resorcinol derivatives which undergo γ-substitution side by side with the normal reaction (B-substitution). Baker (*loc. cit.*), while studying the intramolecular rearrangements of certain resacetophenone derivatives, has made similar observations. Instances of γ-substitution in the case of orcinol exist in literature. Thus it undergoes the Pechmann Reaction with open-chain as well as cyclic B-ketonic esters giving 5-hydroxy-coumarins as observed by Dey[6], and Ahmad and Desai,[7] though malic acid gives the 7-hydroxy-coumarin. By condensing orcinol with glacial acetic acid in the presence of phosphorus oxychloride, Rasinski[8] obtained a ketone which was proved to be 2 : 6-dihydroxy-4-methyl-acetophenone by Ludwinowsky and Tambor[9]. Recently Shah and his co-workers[10] have brought forward the evidence of γ-substitution in resorcinol derivatives, in course of studying Pechmann and Gattermann Reactions. We are busy extending these observations to β-resorcylaldehyde, 4-nitroresorcinol, 4-cyanoresorcinol and orcinol derivatives.

Experimental.

Condensation of acetyl chloride with resorcinol.—

A mixture of resorcinol (5·9 g.), acetyl chloride (3·3 c.c.), anhydrous aluminium chloride (6·9 g.) and nitrobenzene (50 c.c.) was kept at the ordinary

temperature for 24 hours. After decomposing aluminium chloride with dilute ice-cold hydrochloric acid, the nitrobenzene was removed in steam and the precipitate obtained on cooling was collected, dried and crystallised from benzene, when colourless needles melting at 146° were obtained. This was identified as resacetophenone by mixed m.p. with an authentic specimen prepared by Nancki's method (yield 65 per cent.). The aqueous mother-liquor was saturated with salt, and extracted with ether. The gummy residue, on purification through the alkali treatment gave only resacetophenone, and no detectable trace of 2-acetylresorcinol. 4-Ethylresorcinol, on similar condensation with acetyl chloride, gave 2 : 4-dihydroxy-5-ethylacetophenone,[11] and not a trace of the isomeric 2 : 6-dihydroxy-3-ethylacetophenone, which was synthesised as follows :

Synthesis of 2 : 6-*dihydroxy*-3-*ethylacetophenone*.—

(*A*) A solution of methyl 2 : 4-dihydroxy-5-ethylbenzoate (2 g.) and acetic anhydride (1·2 c.c.) in dry nitrobenzene (10 c.c.) was added to the solution of anhydrous aluminium chloride (3·6 g.) in nitrobenzene (30 c.c.) with cautious cooling, and the mixture heated in an oil-bath at 110° for two hours. Excess of aluminium chloride was decomposed by dilute, ice-cold hydrochloric acid, and the nitrobenzene steam distilled off. The solid obtained on cooling crystallised from dilute alcohol in colourless needles melting at 76°. (Found C, 60·4 ; H, 6·1 ; $C_{12}H_{14}O_5$ requires C, 60·5 ; H, 5·9 per cent.)

Methyl 2 : 4-*dihydroxy*-3-*acetyl*-5-*ethylbenzoate* is volatile in steam, and is slightly soluble in petrol and hexane, but very easily soluble in benzene, acetic acid, acetone, and alcohol. Its alcoholic solution gave a dark-violet colouration with aqueous ferric chloride.

Hydrolysis of the above ester with caustic soda to 2 : 6-*dihydroxy*-3-*ethylacetophenone*.—A solution of the ester (1 g.) in 10 per cent. caustic soda (10 c.c.) was heated on sand-bath, for two hours, and acidified with dilute hydrochloric acid on cooling. The precipitated solid was treated with cold sodium bicarbonate solution and the residue cyrstallised from dilute alcohol when yellowish needles melting at 135° were obtained (found C, 66·4 ; H, 6·8 ; $C_{10}H_{12}O_3$ requires C, 66·6 ; H, 6·6per cent.) More of the same ketone was obtained on extracting with ether, the acid mother-liquor saturated with sodium chloride. The alcoholic solution of the ketone gave green colouration with ferric chloride, while it dissolved in concentrated sulphuric acid with a yellow colour.

The semicarbazone, prepared in the usual manner, crystallised from alcohol in needles melting at 252°. (Found C, 55·3 ; H, 6·4.$C_{11}H_{15}O_3N_3$ requires C, 55·7 ; H, 6·3 per cent.) On condensing this ketone with acetic

anhydride in the usual manner, 2 : 6-*diacetyl*-4-*ethylresorcinol* was easily obtained, and this crystallised from dilute alcohol in fine, colourless needles melting at 76°. This was appreciably volatile in steam, and was fairly soluble in petrol, and hexane. Its alcoholic solution gave dark reddish-brown colouration with aqueous ferric chloride. (Found C, 64·6 ; H, 6·2 ; $C_{12}H_{14}O_4$ requires C, 64·9 ; H, 6·3 per cent.)

The semicarbozone crystallised from alcohol in pale-yellow needles melting at 267°.

(*B*) *Preparation of* 6-*ethyl*-7-*hydroxy*-4-*methyl coumarin*.—A mixture of ethylresorcinol (10 g.), acetoacetic ester (10 g.) and 73 per cent. sulphuric acid (50 c.c.) was left for 24 hours at the ordinary temperature, and poured over ice. The crude solid melted at 208°, but on crystallising it from alcohol, white needles melting at 213° were obtained (yield 80–85 per cent.) This coumarin has been prepared by Shah and Samant, and also Chakravarty (*loc. cit.*). The *methyl ether*, prepared by the usual method, crystallised from dilute alcohol in colourless needles melting at 160°. (Found : C, 71·2 ; H, 6·6 ; $C_{13}H_{14}O_3$ requires C, 71·6 ; H, 6·4 per cent.) *The carboethoxy* derivative was obtained by gradually treating the solution of the coumarin (0·2 g.) in 10%, caustic soda (5 c.c.) with ethyl chlorocarbonate (2 c.c.). The precipitated solid, after trituration with alkali, crystallised from dilute alcohol in colourless needles melting at 144°. (Found : C, 64·9 ; H, 6·0 ; $C_{15}H_{16}O_5$ requires C, 65·2 ; H, 5·8 per cent.)

Attempts to bring about the Fries Transformation of the carboethoxy derivative by using either anhydrous aluminium chloride or zinc chloride were not successful.

The acetyl derivative crystallised from dilute alcohol in prismatic needles melting at 143°. (Found : C, 68·1 ; H, 5·9 ; $C_{14}H_{14}O_4$ requires C, 68·3 ; H, 5·7 per cent.)

Synthesis of 8-*acetyl*-7-*hydroxy*-6-*ethyl*-4-*methylcoumarin*.—An intimate mixture of 7-acetoxy-6-ethyl-4-methylcoumarin (10 g.) and finely powdered anhydrous aluminium chloride (25 g.) was heated in an oil-bath at 140–50 for one hour. After decomposing the aluminium chloride with ice-cold hydrochloric acid, the solid was dissolved in sodium carbonate solution, and acidified with concentrated hydrochloric acid. The *coumarin* crystallised from dilute alcohol in straw-coloured needles melting at 139°. The alcoholic mother-liquor on evaporation left a residue (m.p. 105–10°), which was treated with benzene to dissolve the coumarin m.p. 139°. The benzene-insoluble portion proved to be the original 7-hydroxy-6-ethyl-4-methylcoumarin (yield 90 per cent.). (Found : C, 68·4 ; H, 6·0 ; $C_{14}H_{14}O_4$ requires

C, 68·3 ; H, 5·7 per cent.) It dissolved in alkali with a yellow colour, and its alcoholic solution gave blackish-violet colour with ferric chloride. It did not give the acetyl, methyl and carboethoxy derivatives by the usual methods.

The *semicarbazone* did not melt upto 290°.

The Kostanecki Reaction with 4-*methyl*-6-*ethyl* 7-*hydroxy*-8-*acetyl coumarin* and *synthesis of* 4 : 2'-*dimethyl*-6'-*ethyl*-3-*acetyl-coumarino* (7 : 8)-*γ-pyrone.*—The mixture of the coumarin (1 g.), acetic anhydride (7 c.c.) and anhydrous sodium acetate (2·5 g.) was heated in an oil-bath at 175–80° for ten hours. The solid obtained by decomposing the mixture with water was filtered off and treated with 5 per cent. NaOH solution to remove the unchanged coumarin. The *coumarino-γ-pyrone* crystallised from benzene in colourless needles melting at 192°. Its alcoholic solution did not give any colour with $FeCl_3$ solution. It dissolved in sodium hydroxide solution on warming, while its solution in concentrated sulphuric acid was yellow. (Found : C, 69·0 ; H, 5·0; $C_{18}H_{16}O_5$ requires C, 69·2 ; H, 5·1 per cent.)

Hydrolysis of 4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetyl coumarin with* 2*N*-*NaOH.*—A solution of the coumarin (1 g.) in 2N-caustic soda (15 c.c.) was heated on sand-bath under reflux for three hours ; and the cooled solution was acidified with dilute hydrochloric acid. The filtered solid was shaken up with 2 per cent. sodium bicarbonate solution, and the residue crystallised from alcohol, when yellowish needles melting at 135° were obtained. This hydroxy ketone was identical with the one prepared by hydrolysing the condensation product of methyl 2 : 4-dihydroxy-5-ethylbenzoate with acetic anhydride. On condensing it with acetoacetic ester in the presence of conc. H_2SO_4, the coumarin (m.p. 139°) was obtained.

Bromination of 4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetyl-coumarin to* 3-*bromo*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetyl-coumarin.*—The solution of the coumarin (2 g.) in glacial acetic acid (25 c.c.) was gradually treated with a solution of bromine (2·5 c.c.) in glacial acetic acid (10 c.c.). The mixture which became warm immediately, was exposed to bright sunlight for one hour, and the crystalline solid that had separated out was filtered off. The crude solid (m.p. 176°) crystallised from dilute acetic acid in colourless needles melting at 180°. The glacial acetic acid mother-liquor, on dilution with water, gave a further amount of the bromo-compound contaminated with the original product. (Found : Br, 24·8 ; $C_{14}H_{13}O_4Br$ requires Br, 24·6 per cent.)

Hydrolysis of the bromo-coumarin by sodium carbonate solution.—A solution of the bromo-coumarin (2 g.) in 5 per cent. sodium carbonate solution (35 c.c.) was heated on sand-bath under reflux for two hours, cooled and extracted with ether. The ethereal solution gave, on the removal of the

solvent, a solid which crystallised from methyl alcohol in yellowish needles melting at 66°. This was *3-methyl-5-ethyl-6-hydroxy-7-acetyl-coumarone*, because it was also obtained by the decarboxylation of the *coumarilic acid* described below. (Found : C, 71·4 ; H, 6·5 ; $C_{13}H_{14}O_3$ requires C, 71·6 ; H, 6·4 per cent.)

The coumarone was soluble in hot caustic soda. Its alcoholic solution gave green colouration with $FeCl_3$. It could not be methylated, acetylated or carboethoxylated by the usual methods.

The *semicarbazone* crystallised from alcohol in small plates unmelted below 290°. (Found : C, 60·7 ; H, 6·3 ; $C_{14}H_{17}O_3N_3$ requires C, 61·1 ; H, 6·2 per cent.)

The sodium carbonate solution, on acidification with concentrated hydrochloric acid, gave a solid which dissolved almost completely in the cold 2 per cent. sodium bicarbonate solution. On acidification of the filtered solution, 3-methyl-5-ethyl-6-hydroxy-7-acetyl-coumarilic acid melting at 204–06° (decomp.) was obtained. The acid could not be satisfactorily crystallised from any solvent. (Found : C, 63·8 ; H, 5·4 ; $C_{14}H_{14}O_5$ requires C, 64·1 ; H, 5·3 per cent.)

Condensation of methyl-β-resorcylate with acetic anhydride.—The condensation of methyl-β-resorcylate with acetyl chloride at the ordinary temperature did not take place appreciably. The following method using the acetic anhydride was found to give the best yield of methyl 2 : 4-dihydroxy-5-acetyl benzoate after a number of trial experiments.

A solution of anhydrous aluminium chloride (7 g.) in nitrobenzene (60 c.c.) was added to the solution of methyl-β-resorcylate (4 g.) and acetic anhydride (2·5 g.) in nitrobenzene (20 c.c.) and the mixture was heated on water-bath for four hours. After decomposing the aluminium chloride with ice-cold dilute hydrochloric acid, the nitrobenzene was steam-distilled off, and the residue filtered off. On purification through alkali treatment, the crude solid melted at 108–12°. On refluxing with hexane, the hexane-soluble portion crystallised in colourless needles melting at 124° mixed. melting point with anhydrous methyl-β-resorcylate m.p. 124° was 98–100°. (Found : C, 56·8 ; H, 4·8 ; Calc. for $C_{10}H_{10}O_5$: C, 57·1 ; H, 4·9 per cent.)

The hexane-insoluble portion was treated with warm benzene which dissolved a portion of the residue. The solid obtained on the removal of benzene melted at 256°, and was identical with 2 : 4-dihydroxy-5-acetyl-benzoic acid described below.

Hydrolysis of the ester to the acid.—A solution of the ester (1 g.) in normal sodium hydroxide (10 c.c.) was heated on sand-bath under reflux for three

hours. On acidification, the free acid which was identified as 2 : 4-dihydroxy-5-acetyl-benzoic acid crystallised from dilute alcohol in small needles melting at 256°. On heating the acid in an oil-bath at 250°, much of the product sublimed ; and the sublimate (m.p. 146°) was identified as resacetophenone by a mixed melting point (Liebermann and Lindemann (*loc. cit.*).

Condensation of resacetophenone with acetic anhydride.—Resacetophenone did not condense with acetyl chloride at ordinary temperature. The following conditions gave the best result with acetic anhydride.

A solution of anhydrous aluminium chloride (16 g.) in nitrobenzene (100 c.c.) was added to a mixture of resacetophenone (8 g.), acetic anhydride (6 g.) and nitrobenzene (35 c.c.), and the resulting mixture was heated in an oil-bath at 105–10° for two hours. After decomposing the aluminium chloride, nitrobenzene was cautiously steam-distilled off. (Care was taken to see that 2 : 4-diacetyl resorcinol does not volatilise away.) The solid obtained on cooling was filtered off, and the mother-liquor was extracted with ether after saturating it with salt. The solid residue was first boiled with 10 per cent. NaOH, as it was sticky, and the solid recovered after acidification with concentrated hydrochloric acid. The dry solid was first extracted with benzene in which most of it dissolved. The benzene solution, on cooling, deposited 4 : 6-diacetylresorcinol melting at 185° (1·5 g.). The benzene was removed from the mother-liquor, and the residue extracted with hexane. The hexane solution, on cooling, deposited 2 : 4-diacetyl-resorcinol melting at 85–86° (1·5 g.). Authentic specimens of 4 : 6-acetyl-resorcinol and 2 : 4-diacetyl resorcinol were prepared for comparison by following Baker's directions (*loc. cit.*).

Condensation of orcinol with acetyl chloride.—Orcinol (6 g.) dissolved in nitrobenzene (25 c.c.) was added to the solution of aluminium chloride (6·5 g.) in nitrobenzene (50 c.c.) and finally acetyl chloride (5 g.) was cautiously added. After keeping the mixture for 24 hours, and decomposing the aluminium chloride with ice-cold hydrochloric acid, the nitrobenzene was steam-distilled off, and the solid filtered and dried. A considerable portion went in solution in benzene leaving a small residue (0·5 g.) melting at 230–35°. On recrystallisation from dilute alcohol, it melted at 258° and was identified as 4 : 7-dimethyl-5-hydroxy-coumarin by comparison with an authentic specimen.

The benzene solution, on concentration and cooling, deposited glistening plates melting at 159–60°, and was identified as orsacetophenone, by its properties (4 g.). A small amount of orsacetophenone (0·5 g.) was also recovered by extracting with ether the original mother-liquor.

Summary.

Acetyl chloride and acetic anhydride have been condensed with resorcinol 4-ethylresorcinol, methyl β-resorcylate, resacetophenone and orcinol in the presence of anhydrous aluminium chloride and it is found that resacetophenone and orcinol show evidence of γ-substitution side by side with usual β-substitution. Two independent methods of synthesising 2 : 6-dihydroxy-3-ethyl-acetophenone have been worked out, as this unknown ketone was required during the course of the work.

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DIOPHANTISCHE PROBLEME.

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I. Das Gleichungssystem

$$\begin{cases} X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7 = 0 \\ X_1^3 + X_2^3 + X_3^3 + X_4^3 + X_5^3 + X_6^3 + X_7^3 = 0 \\ X_1^5 + X_2^5 + X_3^5 + X_4^5 + X_5^5 + X_6^5 + X_7^5 = 0 \end{cases}$$ in ganzen rationalen Zahlen.

(α) Es seien a und b beliebige ganze Zahlen. Wir setzen nun:

$$\begin{aligned}
A &= a^5 + a^4b - 3a^3b^2 - 11a^2b^3 - 11ab^4 - 3b^5; \\
B &= 2a^4b + 2a^3b^2 - 8a^2b^3 - 8ab^4 - 2b^5; \\
C &= -a^4b - a^3b^2 - 2a^2b^3 - 3ab^4 - b^5; \\
D &= -a^5 - a^4b - 8a^2b^3 - 10ab^4 - 3b^5; \\
E &= -a^5 - 2a^4b + a^3b^2 - 2a^2b^3 - 5ab^4 - 2b^5; \\
F &= -a^4b - 4a^3b^2 - 7a^2b^3 - 4ab^4 - b^5; \\
G &= a^5 + 2a^4b - 2a^3b^2 - 11a^2b^3 - 8ab^4 - 2b^5; \\
H &= -a^5 - 2a^4b - 3a^2b^3 - 6ab^4 - 2b^5; \\
J &= a^4b + 2a^3b^2 - 7a^2b^3 - 10ab^4 - 3b^5; \\
K &= a^5 + 2a^4b - 3a^3b^2 - 12a^2b^3 - 9ab^4 - 2b^5; \\
L &= a^5 + a^4b - 2a^3b^2 - 6a^2b^3 - 4ab^4 - b^5; \\
M &= a^4b - a^3b - 12a^2b^3 - 11ab^4 - 3b^5; \\
N &= -2a^4b - 4a^3b^2 - 6a^2b^3 - 6ab^4 - 2b^5; \\
P &= -a^5 - a^4b + a^3b^2 - 3a^2b^3 - 3ab^4 - b^5.
\end{aligned}$$

(β) Nun gilt die Identität

$$\begin{cases} A + B + C + D + E + F + G = H + J + K + L + M + N + P \\ A^2 + B^2 + C^2 + D^2 + E^2 + F^2 + G^2 = H^2 + J^2 + K^2 + L^2 + M^2 + N^2 + P^2 \\ A^3 + B^3 + C^3 + D^3 + E^3 + F^3 + G^3 = H^3 + J^3 + K^3 + L^3 + M^3 + N^3 + P^3 \\ A^4 + B^4 + C^4 + D^4 + E^4 + F^4 + G^4 = H^4 + J^4 + K^4 + L^4 + M^4 + N^4 + P^4 \\ A^5 + B^5 + C^5 + D^5 + E^5 + F^5 + G^5 = H^5 + J^5 + K^5 + L^5 + M^5 + N^5 + P^5 \\ A^6 + B^6 + C^6 + D^6 + E^6 + F^6 + G^6 = H^6 + J^6 + K^6 + L^6 + M^6 + N^6 + P^6. \end{cases}$$

Setzt man nun $S = \frac{A+P}{2} = \frac{B+N}{2} = \frac{C+M}{2} = \frac{D+L}{2} = \frac{E+K}{2} = \frac{F+J}{2} = \frac{G+H}{2}$, dann bekommt man, wenn man $(S-A)^n + (S-B)^n + (S-C)^n + (S-D)^n + (S-E)^n + (S-F)^n + (S-G)^n = (S-H)^n + (S-J)^n + (S-K)^n + (S-L)^n + (S-M)^n + (S-N)^n + (S-P)^n$ für $n = 1, 2, 3, 4, 5, 6$ setzt und wenn man die Glieder nach der Größe ordnet, Relationen von der Form

(γ) $X_1^n + X_2^n + X_3^n + (-X_4)^n + (-X_5)^n + (-X_6)^n + (-X_7)^n = X_1^n + X_2^n + X_3^n + X_4^n + (-X_3)^n + (-X_2)^n + (-X_1)^n$ für $n = 1, 3, 5$.

Daraus folgt

$$\begin{cases} X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7 = 0 \\ X_1^3 + X_2^3 + X_3^3 + X_4^3 + X_5^3 + X_6^3 + X_7^3 = 0 \\ X_1^5 + X_2^5 + X_3^5 + X_4^5 + X_5^5 + X_6^5 + X_7^5 = 0. \end{cases}$$

(Siehe: "A. Moessner: Zahlentheoretische Untersuchungen" in *The Tohoku Mathematical Journal*, Vol. 39, Part I !).

(δ) *Exempel*: Setzt man $a = 3$, $b = 1$, so bekommt man die Identität $1^n + 109^n + 119^n + 363^n + 492^n + 640^n + 656^n = 24^n + 40^n + 188^n + 317^n + 561^n + 571^n + 679^n$ für $n = 1, 2, 3, 4, 5, 6$, wenn man zu jeder Base der gewonnenen Glieder die Zahl 453 addiert und dann die Glieder nach der Größe ordnet [also eine Identität, wie unter (β) gezeigt]. *NB.*—Die gleichmässige additive oder subtraktive Veränderung der Basen ist hier zülässig, denn: Gilt $A^n + B^n + C^n + D^n + E^n + F^n + G^n = H^n + J^n + K^n + L^n + M^n + N^n + P^n$ für $n = 1, 2, 3, 4, 5, 6$, dann gilt nach einem bekannten Satze der Zahlentheorie auch $(A \pm x)^n + (B \pm x)^n + (C \pm x)^n + (D \pm x)^n + (E \pm x)^n + (F \pm x)^n + (G \pm x)^n = (H \pm x)^n + (J \pm x)^n + (K \pm x)^n + (L \pm x)^n + (M \pm x)^n + (N \pm x)^n + (P \pm x)^n$ für $n = 1, 2, 3, 4, 5, 6$ bei *beliebigem* x.

(ϵ) Aus dem Exempel unter (δ) ergibt sich $S = \frac{1+679}{2} = \frac{109+571}{2} = \frac{119+561}{2} = \frac{363+317}{2} = \frac{492+188}{2} = \frac{640+40}{2} = \frac{656+24}{2} = 340.$

Man bekommt also $339^n + 231^n + 221^n = 23^n + 152^n + 300^n + 316^n$ für $n = 1, 3$ und 5.

II. Das Gleichungssystem

$$\begin{cases} A^2 + B^2 + C^2 = D^2 + E^2 + F^2 \\ A \cdot B \cdot C = D \cdot E \cdot F. \end{cases}$$

Wir bekommen eine allgemeine Lösung dieses Systems, wenn wir setzen

$A = g\,[a\,(a^2 - b^2)\,x^2 - 2\,g\,(a^2 - b^2)\,xy + a\,(g^2 - d^2)\,y^2]$;

$B = ad\,[(a^2 - b^2)\,x^2 - (g^2 - d^2)\,y^2]$;

$C = b\,[g\,(a^2 - b^2)\,x^2 - 2\,a\,(g^2 - d^2)\,xy + g\,(g^2 - d^2)\,y^2]$;
$D = d\,[a\,(a^2 - b^2)\,x^2 - 2\,g\,(a^2 - b^2)\,xy + a\,(g^2 - d^2)\,y^2]$;
$E = bg\,[(a^2 - b^2)\,x^2 - (g^2 - d^2)\,y^2]$;
$F = a\,[g\,(a^2 - b^2)\,x^2 - 2a\,(g^2 - d^2)\,xy + g\,(g^2 - d^2)\,y^2]$ mit beliebigen g, a, b, d, x, y.

Numerisckes Exempel:

Es ergibt $g = 1$, $a = 3$, $b = 2$, $x = 4$, $y = 1$, $d = 5$ die Lösung

$$\begin{cases} 16^2 + 195^2 + 158^2 = 80^2 + 26^2 + 237^2 \\ 16 \cdot 195 \cdot 158 = 80 \cdot 26 \cdot 237. \end{cases}$$

III. Das Gleichungssystem

$$\begin{cases} 4. \quad G^{2n} = K^4 + L^4 + M^4 + 2\,(x^2 + y^2 + z^2) \\ 4. \quad G^{4n} = K^8 + L^8 + M^8 + 2\,(x^4 + y^4 + z^4). \end{cases}$$

(1) Die Formel $2\,(i^2 + 3\,k^2)^v = (2\,ik + 3\,k^2 - i^2)^v + (2\,ik + i^2 - 3\,k^2)^v + (4\,ik)^v$ für $v = 2$ und 4 liefert Identitäten von der Form 2. $A^v = B^v + C^v + D^v$ für $v = 2,\ 4$ (*cf.* A. Moessner: "General Formulæ for Constructing and solving certain simultaneous Equations" in *The Mathematics Student*, 1935, Vol. 3 !), wobei i und k beliebig sind.

(2) Gilt $2 \cdot A^v = B^v + C^v + D^v$ für $v = 2,\ 4$, dann gilt auch

$$\begin{cases} 2 \cdot (A \cdot A^r)^2 = (B \cdot A^r)^2 + (C \cdot A^r)^2 + (D \cdot A^r)^2 \\ 2 \cdot (A \cdot A^r)^4 = (B \cdot A^r)^4 + (C \cdot A^r)^4 + (D \cdot A^r)^4 \text{ fur beliebiges } r. \end{cases}$$

Wir setzen nun $\begin{cases} A \cdot A^r)^2 = G^n \\ A \cdot A^r)^4 = G^{2n} \end{cases}$; $B \cdot A^r = K$; $C \cdot A^r = L$ und $D \cdot A^r = M$.

Dann geht die Gleichung über in

$$\begin{cases} 2 \cdot G^n = K^2 + L^2 + M^2 \\ 2 \cdot G^{2n} = K^4 + L^4 + M^4. \end{cases}$$

Diese Relation muss richtig bleiben, wenn man jede Seite quadriert, es muβ also auch gelten

$$(2 \cdot G^n)^2 = (K^2 + L^2 + M^2)^2 \text{ und } (2 \cdot G^{2n})^2 = (K^4 + L^4 + M^4)^2.$$

Wir bekommen

$$\begin{cases} 4 \cdot G^{2n} = K^4 + L^4 + M^4 + 2\,[(K \cdot L)^2 + (K \cdot M)^2 + (L \cdot M)^2]; \\ 4 \cdot G^{4n} = K^8 + L^8 + M^8 + 2\,[(K \cdot L)^4 + (K \cdot M)^4 + (L \cdot M)^4]. \end{cases}$$

Wir setzen hier $KL = x$; $KM = y$; $LM = z$ und haben die Lösung des vorgelegten Gleichungssystems.

Numerisches Exempel: $i = 1$, $k = 2$ ergibt die Relation $2 \cdot 13^v = 15^v + 7^v + 8^v$ für $v = 2,\ 4$ (*NB* ! Da die Exponenten gerade sind, können negative Vorzeichen unberücksichtigt bleiben). $r = 3$ ergibt das Resultat

$2 \cdot (13 \cdot 13^3)^v = (15 \cdot 13^3)^v + (7 \cdot 13^3)^v + (8 \cdot 13^3)^v$ für $v = 2,\ 4$, also
$2 \cdot (13^4)^v = 32955^v + 15379^v + 17576^v$ für $v = 2,\ 4$.

Durch Quadrieren bekommt man

$$\begin{cases} 4 \cdot 13^{16} = 32955^4 + 15379^4 + 17576^4 + 2\,[(32955 \cdot 15397)^2 + \\ \qquad (32955 \cdot 17576)^2 + (15379 \cdot 17576^2]. \\ 4 \cdot 13^{32} = 32955^8 + 15379^8 + 17576^8 + 2\,[(32955 \cdot 15379)^4 + \\ \qquad (32955 \cdot 17576)^4 + (15379 \cdot 17576)^4]. \end{cases}$$

IV. Das Gleichungssystem

$$a + b + c = d + e + f$$
$$a^2 + b^2 + c^2 = d^2 + e^2 + f^2$$
$$a^3 + b^3 + c^3 = K^3.$$

Wir setzen nach Euler

$a = (r + 3s)(r^2 + 3s^2) - 1$; $b = -(r - 3s)(r^2 + 3s^2) + 1$; $c = -(r + 3s) + (r^2 + 3s^2)^2$; $K = r - 3s - (r^2 + 3s^2)^2$. Dann ist $a^3 + b^3 + c^3 = K^3$.

Nach einem Satze der Zahlentheorie gilt allgemein

$A_1^n + A_2^n + A_3^n + \cdots + A_x^n = (p - A_1)^n + (p - A_2)^n + (p - A_3)^n + \cdots + (p - A_x)^n$ für $n = 1, 2$, wenn $p = \frac{2}{x}$. $(A_1 + A_2 + A_3 \cdots + A_x)$ ist.

Bei der vorgelegten Relation ist $x = 2$, also $p = \frac{2}{3} \cdot (a + b + c)$.

Also gilt $a^n + b^n + c^n = (p - a)^n + (p - b)^n + (p - c)^n$ für $n = 1, 2$. Wir setzen $p - a = d$; $p - b = e$; $p - c = f$ und haben das vorgelegte System gelöst. Man bekommt immer ganzzahlige Lösungen, wenn man die Basen mit 3 multipliziert.

Numerisches Exempel: $r = 2$, $s = 1$ ergibt $a = 34$; $b = 8$; $c = 44$; $K = 50$; gekürzt $17^3 + 4^3 + 22^3 = 25^3$. Um eine ganzzahlige Lösung zu bekommen, setzen wir $51^3 + 12^3 + 66^3 = 75^3 \cdot p = \frac{2}{3} \cdot (51 + 12 + 66) = 86$. Wir bekommen

$$\begin{cases} 51 + 12 + 66 = 35 + 74 + 20 \\ 51^2 + 12^2 + 66^2 = 35^2 + 74^2 + 20^2 \\ 51^3 + 12^3 + 66^3 = 75^3. \end{cases}$$

Exempel mit kleineren Zahlen:

$$\begin{cases} 1 + 6 + 8 = 9 + 4 + 2 \\ 1^2 + 6^2 + 8^2 = 9^2 + 4^2 + 2^2 \\ 1^3 + 6^3 + 8^3 = 9^3. \end{cases}$$

V. Die Gleichung $x^2 - 3y^4 = z^3$ *in ganzen Zahlen.*

Wir setzen $y^2 = t$, dann bekommen wir $x^2 - 3t^2 = z^3$.

Für diese Gleichung besteht folgende Parameterlösung:

$x = m^3 + 9\,mn^2 = m\,(m^2 + 9\,n^2)$

$t = 3\,m^2n + 3\,n^3 = 3\,n\,(m^2 + n^2)$

$z = m^2 - 3\,n^2$. Dann bleibt noch zu lösen:

$3\,n\,(m^2 + n^2) = y^2$.

Hier sind folgende zwei Fälle zu unterscheiden:

$$(\alpha)\begin{cases} m^2 + n^2 = 3\,y'^2 \\ n = y''^2 \end{cases} \qquad (\beta)\begin{cases} m^2 + n^2 = y'^2 \\ n = 3\,y''^2. \end{cases}$$

Die Gleichung $m^2 + n^2 = 3\,y'^2$ ist unmöglich, wie man leicht beweisen kann. Um das System (β) zu lösen, setzt man; $m = p^2 - q^2$ und $n = 2\,pq$. Ausserdem müssen p und q werte annehmen, die durch die nachfolgenden Gleichungspaare gegeben sind

(1) $p = 3\,r^2$ $\qquad q = 2\,s^2$

(2) $p = 2\,r^2$ $\qquad q = 3\,s^2$

(3) $p = 6\,r^2$ $\qquad q = s^2$

(4) $p = r^2$ $\qquad q = 6\,s^2$.

Für den Fall (1) zum Beispiel findet man die Formeln:

$$\begin{cases} x = (9\,r^4 - 4\,s^4)\,[(9\,r^4 - 4\,s^4)^2 + 81\,(2\,rs)^4] \\ y = 6\,rs\,(9\,r^4 + 4\,s^4) \\ z = (9\,r^4 - 4\,s^4)^2 - 27\,(2\,rs)^4 \end{cases}$$

r und s sind beliebige ganze Zahlen.

Der Leser stellt selbst leicht die Formeln für die anderen Fälle auf.

Exempel: $r = 2$, $s = 1$ ergibt nach Vereinfachung $88235^2 - 3 \cdot 222^4 = 793^3$.

VI. Ganzzahlige Lösung zu $x^4 + y^2 = z^3$.

Wir gehen aus von der Identität

$(m^3 - 3\,mn^2)^2 + (3\,m^2n - n^3)^2 = (m^2 + n^2)^3$. Wir verwandeln nun den Ausdruck $m^3 - 3\,mn^2 = m\,(m^2 - 3\,n^2)$ in ein Quadrat, indem wir jeden Faktor dieses Produktes in ein Quadrat verwandeln, und wir gelangen so zu einer Identität, die eine unendliche Anzahl von Lösungen der vorgelegten Gleichung ergibt:

$$[(r^2 + 3\,s^2)\,(r^4 - 18\,r^2s^2 + 9\,s^4)]^4 + [4\,rs\,(r^2 - 3\,s^2)\,(3\,r^8 + 20\,r^6s^2 + 258\,r^4s^4 + 180\,r^2s^6 + 243\,s^8)]^2 = (r^8 + 28\,r^6s^2 - 42\,r^4s^4 + 252\,r^2s^6 + 81\,s^8)^3.$$

Exempel.—$r = 2$, $s = 1$ ergibt $329^4 + 57112^2 = 2465^3$.

VII. Ganzzahlige Lösung zu $x^4 + y^2 = z^6$.

Wir gehen aus von $(m^3 + mn^2)^2 + (m^2n + n^3)^2 = (m^2 + n^2)^3$. Wenn wir den Ausdruck $m^3 + mn^2 = m\,(m^2 + n^2)$ in ein Quadrat verwandeln wie unter VI,

so wird aus dem Kubus auf der 2. ten Gleichungsseite eine sechste Potenz. Nach Ausführung der Rechnungen ergibt sich die Identität

$$[(r^2 - s^2)(r^4 + 6r^2s^2 + s^4)]^4 + [4rs(r^2 + s^2)(r^4 + 6r^2s^2 + s^4)^2]^2 = (r^4 + 6r^2s^2 + s^4)^6.$$

Exempel.— $r = 2$, $s = 1$ ergibt $123^4 + 67240^2 = 41^6$.

VIII. Allgemeine ganzzahlige Lösung des Systems

$$\begin{cases} x^2 + xy + y^2 = z^3 & (1) \\ x + y \qquad = t^2 & (2) \end{cases}$$

Fur die Gleichung (1) haben wir die Parameterlösung $x = m^3 - 3mn^2 - n^3$; $y = 3m^2n + 3mn^2 = 3mn(m + n)$; $z = m^2 + mn + n^2$.

Es bleibt aufzulösen $m^3 + 3m^2n - n^3 = t^2$.

Man kennt eine Paramterlösung (2 Parameter) der allgemeineren Gleichung $m^3 + am^2n + bmn^2 + cn^3 = t^2$ (*Siehe zum Beispiel Carmichael, Analyse indéterminée*, 1929, Seite 58 und 59).

Durch Anwendung der bekannten Formeln wird gefunden:

$$m = \alpha^2 - 8p^2q - 12p^2$$
$$n = 4\alpha pq - 4p^2.$$

α ist eine Funktion von p und q. Hier der Ausdruck von α:

$$\alpha = -9p - 6pq - pq^2$$
$$t = \alpha^3 + 6\alpha^2p(q + 3) + 12\alpha p^2(q + 2) + 8p^3(1 - 3q^2 - q^3).$$

Man kann t auch als Funktion von p und q allein darstellen.

Exempel. —$p = 1$, $q = 2$, $m = 597$, $n = -204$ ergibt.

$$\begin{cases} x = 146731581 \\ y = -143588052 \\ z = 276237 \\ t = 1773. \end{cases}$$

DERIVATIVES OF SALICYLIC ACID.

Part XIII. Chlorosalicylic Acids and Their Methyl Ethers.

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(Communicated by Dr. T. S. Wheeler, Ph.D., D.Sc., F.Inst.P., F.I.C., M.I.chem.E.)

3-Substituted salicylic acids are difficult to obtain by direct substitution; the orienting influence is favourable to position 5. Chlorination[1] of salicylic acid has so far given a mixture consisting mainly of 5-chlorosalicylic acid, and small quantities of 3-chloro-and 3 : 5-dichlorosalicylic acids and chlorophenols; no conditions were known which would give each of these substances alone and separately. The methyl ethers of these acids had also not received proper attention; that of 3-chlorosalicylic acid being yet unknown, and those of 5-chloro- and 3 : 5-dichlorosalicylic acids[2] obtained indirectly from 2-methyl-4-chlorophenyl methyl ether and 2-methyl-4 : 6-dichlorophenyl methyl ether.

As the amides of these acids were required for some other work, convenient methods had to be worked out for the preparation of the above acids, which together with some new derivatives form the subject-matter of the present paper.

3-*Chlorosalicylic acid*.—This acid has now been prepared in good yield by two different methods. Sulphonic acid group in 5-sulphosalicylic acid is unstable and can be substituted with hydrogen by superheated steam.[3] This acid when chlorinated gave 3-*chloro*-5-*sulphosalicylic acid* which on desulphonation at 160°–70° gave 3-chlorosalicylic acid.

In previous work with chloralsalicylamide, it has been found that the substitution of carboxyl group by chloralamide group changes the main orienting influence from position 5 to position 3. In agreement with this observation a good yield of *chloral*-3-*chlorosalicylamide* is obtained by the chlorina-

[1] Heubner and Brenken, *Ber.*, 1873, **6**, 174; Lassar-Cohn and Schultze, *ibid.*, 1905, **38**, 3300; Ullmann and Kopetschni, *ibid.*, 1911, **44**, 428.

[2] Paratoner and Condorelli, *Gaz.*, 1898, **281**, 211–12; Martini, *ibid.*, 1899, **29**, II, 62.

[3] Meldrum and Shah, *J.C.S.*, 1923, **123**, 1986; Hirwe and Patil, *Proc. Ind. Acad. Sci.*, 1937, **5** (4), 321–25.

tion of chloralsalicylamide, which yields 3-chloro-salicylic acid in good quantity on hydrolysis.

Methylation of the chloroacid with dimethyl sulphate and concentrated alkali affords a good yield of the *methyl ether*, hitherto unknown.

5-*Chlorosalicylic acid.*—This acid is obtained alone and not in a mixture, as obtained by previous workers[4] if the rate of passing chlorine and the temperature is controlled, as described in the experimental section.

3 : 5-*Dichlorosalicylic acid.*—The rate of passing chlorine is not very important in this case. Chlorination of salicylic acid at 0°–5° gives pure dichloro acid.

The methyl ethers of the above two acids have been obtained by chlorination of the corresponding 2-methoxy-benzoic acids ; they could not be obtained by the direct methylation of the acids.

The *amides* of some of the above compounds have been prepared by the usual methods.

Experimental.

3-*Chlorosalicylic acid* has been prepared by two different methods.

Method I.—By using (*a*) molecular chlorine or (*b*) nascent chlorine. (*a*) Chlorine (35 g., 1 mol.) was slowly passed at 0°–5° into a glacial acetic acid solution of 5-sulphosalicylic acid (100 g.). The mixture was kept at room temperature overnight during which time, much hydrogen chloride was evolved and a sticky mass separated. This was filtered on glass-wool, and dried on a porous plate. It was then dissolved in a little hot water to which syrupy phosphoric acid was added to raise the boiling point ; superheated steam was passed in the liquid mass, the temperature finally reaching 170°. On cooling, 3-chlorosalicylic acid separated and was filtered off and the filtrate repeatedly heated with superheated steam as before until no further yield of 3-chlorosalicylic acid was obtained. The solid was collected, washed with water and crystallised from dilute alcohol : white needles, m.p. 180°–182° (178°–Varnholt[5] ; 180°–Anschutz, Anspach[6]) : yield about 72 per cent. It gave with ferric chloride an intense violet colouration.

Part of the 3-chloro acid probably decomposes to chlorophenol, as indicated by the smell, during desulphonation. (*b*) Powdered potassium permanganate (17 g.) was added slowly with constant stirring to concentrated hydrochloric acid (200 c.c.) in which was dissolved 5-sulphosalicylic acid

[4] Heubner and Brenken and others (*loc. cit.*).

[5] *J. Prak. Chem.*, 1887, **36** (2), 22.

[6] *Ann.*, 1906, **346**, 312.

(50 g.). The reaction mixture was kept overnight and the resulting clear solution was concentrated and then heated in a strong round-bottomed flask with addition of syrupy phosphoric acid. Superheated steam was then passed into the liquid mass for about an hour, the temperature finally reaching 170°. The smell of chlorophenol was observed also in this process. The operation was stopped when a solid product started separating. The solid was washed with water to remove potassium and manganese salts; the chloro-acid crystallised from alcohol in white needles: m.p. and mixed m.p. with product from (*a*) 180–182°.

Chloral-3-chlorosalicylamide (*chlorination of chloralsalicylamide*).—Chlorine (5 g.) was slowly passed into a solution of chloralsalicylamide (20 g.) in glacial acetic acid, keeping the temperature below 15°. When the required amount of chlorine had been absorbed, the solution was kept overnight at room temperature. No solid had separated by next day. On dilution with water a pinkish powder (18 g.) was precipitated which was filtered. The crude product, m.p. 132–136°, on crystallisation from alcohol gave colourless needles m.p., 159–160°: the alcoholic solution gave a red colouration with ferric chloride.

(Found: N, 4·5; Cl, 44·7; $C_9H_7O_3NCl_4$ requires N, 4·4; Cl, 44·5 per cent.)

3-*Chlorosalicylic acid* (*Hydrolysis of Chloral-3-chlorosalicylamide*).—Chloral-3-chlorosalicylamide (20 g.) was dissolved in sodium hydroxide (10 per cent. 200 c.c.) and the solution refluxed on a sand-bath for about six hours. After cooling, the solution was acidified with dilute hydrochloric acid, when a paste resulted. It was washed with water several times until it solidified. The solid crystallised from dilute alcoholic white needles with m.p. 180–81°. The mixed melting point of this substance with that obtained by *Method I* above showed no lowering. Yield about 86 per cent.

Potassium-3-chlorosalicylate crystallised from water in needles. (Found: K, 18·9; $C_7H_4O_3ClK$ requires K, 18·5 per cent.).

Calcium-3-chlorosalicylate—crystallised from water in white plates. (Found: Ca, 9·0; H_2O, 12·2; $C_{14}H_8O_6Cl_2Ca$, $3H_2O$ requires Ca, 9·2; H_2O, 12·4 per cent.)

Silver-3-chlorosalicylate—crystallised from water in minute needles turning dark on exposure. (Found: Ag, 38·4; $C_7H_4O_3ClAg$ requires Ag, 38·6 per cent.)

3-*Chlorosalicylamide : Method I.*—A mixture of methyl-3-chlorosalicylate (20 g.) and liquor ammonia (200 c.c.; D. 0·888) was put in a spring-stoppered bottle and mechanically shaken for six hours when a clear

solution was obtained which on evaporation on a water-bath gave a solid. It was triturated with dilute hydrochloric acid, filtered, washed and dried. (It is soluble in hot water, alcohol, acetone and acetic acid.) The amide crystallised from dilute alcohol in white needles, m.p. 174–175° ; it gave as violet-red colouration with ferric chloride. (Found : Cl, 20·8 ; $C_7H_6O_2NCl$ requires Cl, 20·7 per cent.)

Method II.—A mixture of 3-chlorosalicylic acid (10 g.) and phosphorous pentachloride (12 g.) suspended in low-boiling petroleum ether was refluxed at 30–40° for four hours (Anschutz and Anspach[7]), the cool reaction mixture was poured into liquor ammonia (D· 0·888), kept cool by surrounding ice, with constant stirring. The solid (8·5 g.) crystallised from dilute alcohol : prisms, m.p. 174–176°. Mixed melting point with the amide prepared by *Method I* above showed no lowering.

5-*Chlorosalycilic acid.*—Salicylic acid (14 g.) was dissolved in glacial acetic acid and the container surrounded with ice. Into the ice-cold solution chlorine (7 g.) was gradually passed, so that the bubbles could be counted (about 60–70 bubbles per minute). The resulting solution was allowed to stand overnight at the room temperature, during which hydrogen chloride was evolved. On diluting the solution with water, a solid was obtained which crystallised from dilute alcohol in fine needles, m.p. 172–173° ; yield 15 g. ; it gave with alcoholic ferric chloride a violet colouration (m.p., 167·5°—Beilstein[8] ; 172·5°—Huebner, Brenken[9] ; 176°—Lassar-Cohn, Schultze[10]).

3 : 5-*Dichlorosalicylic acid.*—Salicyclic acid (14 g., 1 mol.) was dissolved in glacial acetic acid and the container surrounded with ice. Into the ice-cold solution, chlorine (14 g., 2 mols.) was slowly passed, the rate of bubbling chlorine did not require to be specially controlled as in the above experiment. The resulting solution was kept overnight at room temperature and then heated on a water-bath for about an hour to complete the reaction. Hydrogen chloride was profusely evolved. The reaction mixture gave a solid on dilution with water ; this crystallised from dilute alcohol in thick needles, m.p. 219–220° ; yield 16·5 g. ; it gave with alcoholic ferric chloride a reddish-violet colouration (m.p. 219·5°—Martini[11]; 223°—Lassar-Cohn, Schultze[12]).

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[7] *Ibid.*

[8] *Ber.*, 1875, **8**, 816 ; *Ann.*, 1875, **179**, 285.

[9] *Ibid.*, 1873, **6**, 174.

[10] *Ibid.*, 1905, **38**, 3300.

[11] *Gaz.*, 1899, **29**, II, 62.

[12] *Ber.*, 1905, **38**, 3300.

Calcium-3 : 5-*dichlorosalicylate*—crystallised from water in white plates. Found : Ca, 7·4 ; H_2O, 14·0 ; $C_{14}H_6O_6Cl_4Ca$, $4H_2O$ requires Ca, 7·6 ; H_2O, 13·7 per cent.)

3-*Chloro*-2-*methoxybenzoic acid*.—3-Chlorosalicylic acid (17 g.) was dissolved in cold potassium hydroxide (75 c.c.—40 g. KOH in 150 c.c. H_2O) and dimethyl sulphate (100 g.) gradually added with constant shaking and cooling under tap. It was then kept overnight and then heated on a water-bath for half an hour, when further quantity of potassium hydroxide (75 c.c. remaining from above) was added and the heating continued for quarter of an hour more. The cooled solution on acidification gave a solid (16 g.) which crystallised from alcohol : white needles ; m.p. 120–21° : it gave no colouration with alcoholic ferric chloride. (Found : equivalent weight, 187·4 ; Cl, 19·1 ; $C_8H_7O_3Cl$ requires equivalent weight, 186·5 ; Cl, 19·0 per cent.) It is soluble in alcohol, acetone, benzene and acetic acid.

Sodium-3-*chloro*-2-*methoxybenzoate*—crystallised from water : needles. (Found : Na, 10·4 ; H_2O, 8.1 ; $C_8H_6O_3ClNa$, H_2O requires Na, 10·2 ; H_2O, 8·0 per cent.)

Barium-3-*chloro*-2-*methoxybenzoate*—crystallised from water : white needles. (Found : Ba, 23·8, 23·8 ; $C_{16}H_{12}O_6Cl_2Ba$, $4H_2O$ requires Ba, 23·6 per cent.)

Silver-3-*chloro*-2-*methoxybenzoate*.—Difficultly soluble in hot water : darkens. (Found : Ag, 37·1 ; $C_8H_6O_3ClAg$ requires Ag, 36·8 per cent.)

3-*Chloro*-2-*methoxybenzamide*.—A mixture of 3-chloro-2-methoxybenzoic acid (6 g.) and phosphorous pentachloride (7 g.) was treated as above, until a yellowish-white solid (5 g.) was obtained. It crystallised from alcohol : flakes, m.p., 99–100° : it gave no colouration with alcoholic ferric chloride. (Found : Cl, 19·3 ; $C_8H_8O_2NCl$ requires Cl, 19·1 per cent.) It is soluble in alcohol, acetone, benzene and acetic acid.

5-*Chloro*-2-*methoxybenzoic acid*.—2-Methoxybenzoic acid (14 g.) was dissolved in glacial acetic acid and the solution kept cool by surrounding ice whilst chlorine (7 g.) was passed into it. The resulting solution was allowed to stand overnight at room temperature. On dilution a solid was obtained (15·5 g.) which crystallised from dilute alcohol : white needles, m.p. 80–81° ; it gave no colouration with alcoholic ferric chloride (m.p. 81–82°—Peratoner, Condorelli[13]).

Silver-5-*chloro*-2-*methoxybenzoate*—crystallised from water : minute needles turning brownish. (Found : Ag, 36·9 ; $C_8H_6O_3ClAg$ requires Ag, 36·8 per cent.)

[13] *Gaz.*, 1898, **28**, I, 211.

5-*Chloro*-2-*methoxybenzamide*.—A mixture of 5-chloro-2-methoxybenzoic acid (6 g.) and phosphorous pentachloride (7 g.) was treated as above. A solid (5 g.) was obtained. It crystallised from alcohol : prisms, m.p. 137–138° ; it gave no colouration with alcoholic ferric chloride. (Found : Cl, 19·2 ; $C_8H_8O_2NCl$ requires Cl, 19·1 per cent.) It is soluble in alcohol, acetone, benzene and acetic acid.

3 : 5-*Dichloro*-2-*methoxybenzoic acid*.—2-Methoxybenzoic acid (15 g.) was dissolved in glacial acetic acid and the solution kept cool by surrounding ice, whilst chlorine (15 g.) was passed into it. The resulting solution was kept overnight at room temperature. Next day a solid (11 g.) had separated which was filtered off, washed with acetic acid and then with water and dried. It crystallised from alcohol : white prisms, m.p. 166–167°. A further quantity (4 g.) of the substance was recovered by diluting the mother-liquor with water. It gave no colouration with alcoholic ferric chloride (m.p. 166·5–167° Martini[14]).

Sodium-3 : 5-*dichloro*-2-*methoxybenzoate*—crystallised from water : white plates. (Found : Na, 8·0 ; H_2O, 13·2 ; $C_8H_5O_3Cl_2Na$, $2H_2O$ requires Na, 8·2 ; H_2O, 12·90 per cent.)

Barium-3 : 5-*dichloro*-2-*methoxybenzoate*—crystallised from water : needles. (Found : Ba, 20·3 ; H_2O, 13·2 ; $C_{16}H_{10}O_6Cl_4Ba$, $5H_2O$ requires Ba, 20·5 ; H_2O, 13·5 per cent.)

Silver-3 : 5-*dichloro*-2-*methoxybenzoate*.—Very difficultly soluble in water : turns grey. (Found : Ag, 33·1 ; $C_8H_5O_3Cl_2Ag$ requires Ag, 32·9 per cent.)

3 : 5-*Dichloro*-2-*methoxybenzamide*.—A mixture of 3 : 5-dichloro-2-methoxybenzoic acid (20 g.) and phosphorous pentachloride (25 g.) was treated as above, when a solid (19·5 g.) was obtained. It crystallised from alcohol : white prisms ; m.p. 152–153° ; it gave no colouration with alcoholic ferric chloride. (Found : N, 6·0 ; $C_8H_7O_2NCl_2$ requires N, 6·4 per cent.) It is soluble in alcohol, acetone, benzene and acetic acid.

The authors are thankful to Dr. R. C. Shah for his help.

[14] *Ibid.*, 1899, **29**, II, 62.

NUCLEAR METHYLATION OF RESACETOPHENONE.

Preparation of 3-Methylresacetophenone and Its Derivatives.

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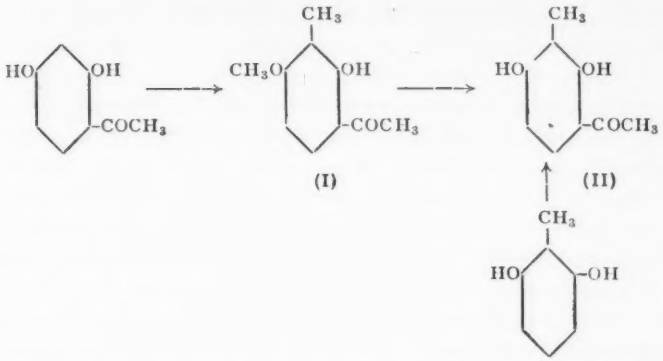
The reactions of resacetophenone are controlled by the existence of chelation as a consequence of which the aromatic double bonds have a tendency to get fixed. Baker and Lothian[1] have shown that 2-hydroxy-4-allyloxyacetophenone on heating gives 3-allylresacetophenone thereby indicating that the 3-position is the reactive one. A similar result has been obtained by Shah and others in the condensation of resacetophenone with ethyl acetoacetate in the presence of aluminium chloride in ether solution, the formation of the coumarin ring involving the 3-position.[2] Under the same conditions hydrogen cyanide introduces an aldehyde group in the 3-position in resacetophenone and its analogues.[3]

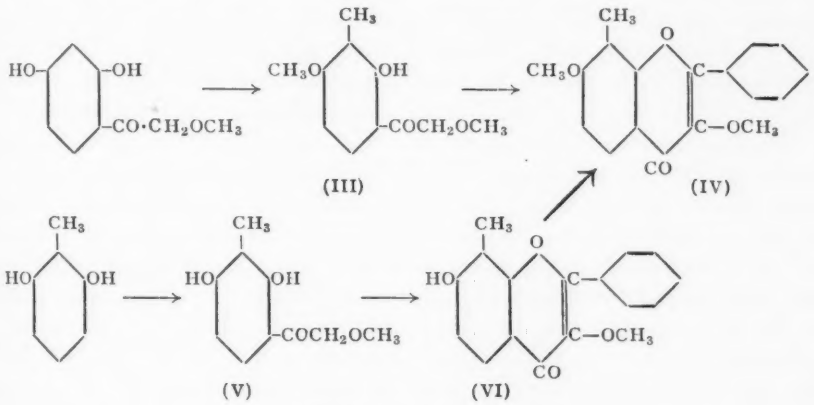
Since 3-methylresacetophenone and its derivatives were required as reference compounds and starting materials in connection with other work in progress in these laboratories and their preparation *via* 2-methyl-resorcinol is rather round about the nuclear methylation of resacetophenone and ω-methoxy-resacetophenone has now been studied.

Resacetophenone formed 2-hydroxy-3-methyl-4-methoxy-acetophenone (I) on treatment with methyl iodide and methyl alcoholic potash. This underwent demethylation to give 3-methyl-resacetophenone (II). The constitution of this compound was established by its synthesis from 2-methylresorcinol (Perkin[4]; Rangaswami and Seshadri[5]) by condensation with acetonitrile. With regard to the progress of this methylation resacetophenone resembles the esters of β-resorcylic acid, the same factors obviously being involved in both cases.

The work has been repeated with ω-methoxyresacetophenone[6] and in this connection the assumption that the hydroxy group which undergoes etherification is the one present in the 4th position and not the one in the 2nd position has been substantiated. The product of nuclear methylation (III) easily undergoes condensation with sodium benzoate and benzoic anhydride according to the procedure developed by Allan and Robinson[7]



and yields a flavone which has been found to be 3 : 7-dimethoxy-8-methyl-flavone (IV). The production of a flavone is itself sufficient proof that the 2-hydroxy group has not been affected by the process of methylation. The identity of (IV) has however been established by its synthesis starting from 2-methylresorcinol. By condensation with methoxyacetonitrile ω-methoxy-3-methyl-resacetophenone (V) was obtained which with sodium benzoate and benzoic anhydride gave rise to 3-methoxy-7-hydroxy-8-methyl-flavone (VI) which subsequently underwent methylation easily to give (IV).



Experimental.

Nuclear methylation of resacetophenone :—2-hydroxy-3-methyl-4-methoxy-acetophenone.—A solution of resacetophenone (2 g.) in methyl alcoholic potash containing 15 c.c. of anhydrous methyl alcohol and 2·6 g. of caustic potash was cooled in freezing-mixture and treated with ice-cold methyl

iodide (4·2 c.c.) all at once. The mixture was well shaken to render it homogeneous and the container left well stoppered in the ice-bath to assume laboratory temperature slowly. After standing overnight the mixture which had deposited a little solid was gently boiled under reflux in a water-bath for 7 hours and then poured into excess of ice-water (150 c.c.). The slightly pasty mass that separated overnight was filtered, washed with water and then macerated with cold dilute alkali when nearly half of it went into solution leaving the remainder as a clean solid. This insoluble portion when filtered and washed with water melted indefinitely in the neighbourhood of 80° and on crystallisation from alcohol gave 2-hydroxy-3-methyl-4-methoxy-acetophenone in the form of stout needles and micacious plates melting at 82–3°. (Found : C, 66·5 ; H, 7·0 ; OCH_3, 17·3 ; $C_{10}H_{12}O_3$ requires C, 66·7 ; H, 6·7 ; OCH_3, 17·2 per cent.). Yield 0·6 g. The compound was easily soluble in the common organic solvents and gave a greenish blue colour with alcoholic ferric chloride.

Demethylation of above to produce 3-methylresacetophenone.—The above compound (0·5 g.) was dissolved in a mixture of phenol (0·5 g.) and acetic anhydride (0·5 c.c.) and gently boiled for half an hour with hydriodic acid (sp. gr. 1·70 ; 8 c.c.). The resulting liquid was diluted with water (20 c.c.) and repeatedly ether-extracted. The combined ether-extract was shaken with sodium bicarbonate solution to remove the acetic acid and then washed with a little water. On evaporation of the solvent a dark-coloured oil was left behind. This was stirred thrice with small quantitites of water which was then thrown away, so as to remove most of the phenol used. The residual oil was then dissolved in alcohol and allowed to crystallise whereby a compound melting from 141 to 146° was obtained. This on two further crystallisations from benzene gave 3-methylresacetophenone in the form of plates and needles melting at 154–5° and was found to be identical with the specimen prepared from 2-methylresorcinol (see below).

3-Methylresacetophenone from 2-methylresorcinol.—A solution of 2-methylresorcinol (1 g.) in absolute ether (25 c.c.) was treated with pure acetonitrile (0·8 g.) and anhydrous zinc chloride (0·5 g.) and saturated with dry hydrogen chloride. The current of the gas was stopped at the end of two hours and the mixture left overnight. The clear solution that was obtained on the addition of water (25 c.c.) was shaken with ether to remove unchanged reactants. The pale yellow aqueous solution containing the ketimine-hydrochloride was heated for one hour in a boiling water-bath and then cooled when the ketone separated in the form of a crystalline powder. On recrystallising from methyl alcohol it was obtained as colourless needles and rectangular plates melting at 156–7°. (Found : C, 64·6 ; H, 6·1 ; $C_9H_{10}O_2$

requires C, 65·1 ; H 6·0 per cent.). It gave a violet colour with alcoholic ferric chloride. A mixed melting point with the sample obtained starting from resacetophenone showed no depression.

2-*Hydroxy*-3-*methyl*-ω : 4-*dimethoxyacetophenone*.—The nuclear methylation of ω-methoxyresacetophenone was carried out according to the same procedure as was adopted in the case of resacetophenone. The reaction was more easy and the product was obtained pure more readily. The solution of the ω-methoxy ketone in alcoholic potash which set to a thick cake at the temperature of the freezing-bath was diluted with enough anhydrous methyl alcohol to enable uniform mixing and shaking, before methyl iodide was added. As the methylation proceeded big crystals of potassium iodide separated from the solution. When after refluxing for 7 hours the mixture was poured into water and left overnight the precipitated solid was found to be only slightly sticky and to melt rather sharply at 96–8°. After crystallisation from alcohol in which it was easily soluble the 3-methyl-4-methoxy ketone came down as long woolly fibres melting at 109°. (Found : C, 62·4 ; H, 6·5 ; $-OCH_3$, 29·2 ; $C_{11}H_{14}O_4$ requires C, 62·9 ; H, 6·7 ; $-OCH_3$, 29·5 per cent.).

The substance appeared as long rectangular rods under the microscope, gave a pinkish brown colour with alcoholic ferric chloride and was insoluble in cold dilute alkali. During combustion it melted smoothly to a brown liquid, after which it decomposed to give a dark oily product which proved very refractory. Yield of the twice-crystallised product was 0·6 g. from 2 g. of ω-methoxyresacetophenone.

3 : 7-*Dimethoxy*-8-*methylflavone from the above ketone*.—An intimate mixture of the ketone (1 g.), sodium benzoate (1·5 g.) and benzoic anhydride (4 g.) was heated in an oil-bath at 200° for 4 hours under a pressure of about 40 mm. of mercury. The residue was treated with a large excess of water containing a little sodium carbonate and left for some hours in order to remove the excess of benzoic anhydride. The aqueous portion was decanted off and the solid left behind treated again in the same fashion with excess of water and carbonate. A dark coloured oil remained which when dissolved in alcohol and left for some days deposited needles with a glistening yellow colour and melting at 143–45°. When recrystallised from alcohol the flavone melted at 145–46° and had the appearance of stout rectangular prisms under the microscope. (Found : C, 72·9 ; H, 5·3 ; $C_{18}H_{16}O_4$ requires C, 73·0 ; H, 5·4 per cent.). A mixed melting point showed it to be identical with the specimen prepared from 2-methylresorcinol as described below.

3-*Methyl*-ω-*methoxyresacetophenone*.—The preparation of this compound from 2-methylresorcinol was very similar to that of 3-methylresaceto-

phenone. Methoxyacetonitrile (b.p. 119–23°) was used instead of acetonitrile and the condensation took place even without the addition of anhydrous zinc chloride, the ketimine hydrochloride separating in a crystalline form in about 4 hours from the commencement of the reaction. When the mixture was treated with water the next day and the aqueous solution after shaking with ether was heated in a boiling water-bath the required ketone separated in the form of a crystalline powder. After recrystallisation from alcohol it came out as rectangular and hexagonal prisms melting at 203–5°. (Found : C, 60·8 ; H, 6·4 ; $C_{10}H_{12}O_4$ requires C, 61·2 ; H, 6·1 per cent.). The compound was fairly soluble in hot water and easily in the common organic solvents and gave a dark violet colour with alcoholic ferric chloride.

3-*Methoxy*-7-*hydroxy*-8-*methylflavone from the above ketone.*—An intimate mixture of the ketone (0·4 g.), sodium benzoate (1 g.) and benzoic anhydride (4 g.) was heated under reduced pressure for 4 hours in an oil-bath at 190°. The product was then refluxed for half an hour with 10 per cent. alcoholic potash (30 c.c.) to hydrolyse the 7-benzoyloxy compound first formed. Most of the alcohol was then distilled off, the residue diluted with water and the clear solution saturated with carbon dioxide. The required 7-hydroxy flavone was thus precipitated and when crystallised from alcohol was obtained in the form of rectangular plates melting at 252–3°. (Found : C, 71·9 ; H, 5·4 ; $C_{17}H_{14}O_4$ requires C, 72·3 ; H, 5·0 per cent.). It did not give any colour with alcoholic ferric chloride.

3 : 7-*Dimethoxy*-8-*methylflavone from the above.*—The 7-hydroxy-flavone (0·2 g.) was dissolved in dry acetone (15–20 c.c.) and heated under reflux on a water-bath for 16 hours with a large excess of methyl iodide (2 c.c.) and anhydrous potassium carbonate (0·4 g.). The residue after evaporation of the solvent was treated with acidulated water and the water-insoluble portion filtered. The precipitate was dissolved in a slight excess of alcohol and the solution filtered from insoluble matter and allowed to stand. Beautiful crystals separated in the course of a few days which after filtering and washing with a few drops of cold alcohol melted at 135–6°. After another crystallisation from aqueous alcohol the methyl ether was obtained as pale yellow needles which melted at 141–2° and appeared as rectangular rods under the microscope. (Found : C, 72·8 ; H, 5·6 ; $C_{18}H_{16}O_4$ requires C, 73·0 ; H, 5·4 per cent.). It was identical in all respects with the one prepared from 2-hydroxy-3-methyl-ω : 4-dimethoxyacetophenone.

Summary.

The methylation of resacetophenone and its ω-methoxy derivative using methyl iodide and methyl alcoholic potash has been studied. The former

gave 2-hydroxy-3-methyl-4-methoxyacetophenone the constitution of which was established by demethylation to 3-methylresacetophenone and comparison with a specimen prepared from 2-methylresorcinol. In the same way ω-methoxyresacetophenone gave 2-hydroxy-3-methyl-ω : 4-dimethoxyacetophenone which was subsequently converted to 3 : 7-dimethoxy-8-methylflavone. The identity of this flavone was proved by its synthesis from 2-methyl-resorcinol.

It is concluded that under the above conditions resacetophenone undergoes nuclear methylation in the 3-position and that the hydroxyl group in the 4th position gets etherified.

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A FINE ADJUSTMENT DEVICE FOR USE WITH THE MICRO-DUMAS APPARATUS.

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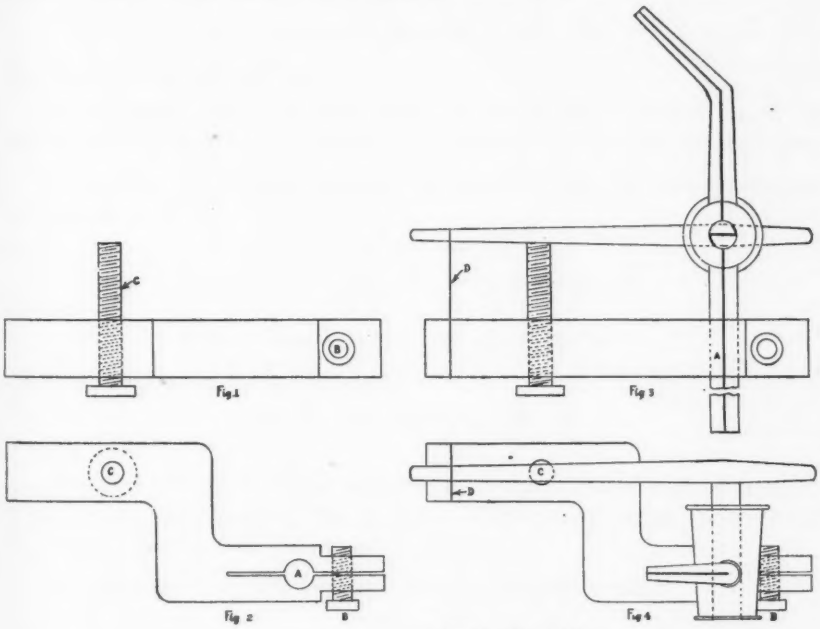
It is well known that in the determination of nitrogen in organic compounds by the method of Pregl (*Quantitative Organic Micro-Analysis* by Pregl—2nd and 3rd English editions) the accuracy of the experiment depends on the rate of combustion of the compound, which is controlled by observing the rate of entry of gas bubbles into the nitrometer past the mercury seal. To obtain a good value not only should the preliminary combustion of the compound be carried out at the optimum rate which gives rise to not more than two bubbles in every three seconds, but the subsequent washing out of the products of combustion from the combustion tube into the nitrometer by means of carbon dioxide from the Kipp should be done so carefully that a gas rate of two bubbles in three seconds is not exceeded even for a few seconds. The latter operation requires considerable experience as a higher gas rate invariably gives higher values for nitrogen than according to the theory.

For the delicate manipulation of the stop-cock in the connecting piece various devices have been tried in the past, the most satisfactory being the provision of the stop-cock with a long handle so that by the application of gentle pressure to the tip of the handle small rotations of the barrel can be effected. The cutting of shallow channels about 4 mm. long on the surface of the barrel at either end of the main bore has considerably added to the value of the long handle, and ensures accurate results to the careful and diligent worker (*loc. cit.*).

The above combination suffers from one or two drawbacks. The barrel of the stop-cock must be greased to a certain optimum extent. While over-greasing fills up part of the channel and makes the stop-cock turn round of its own accord owing to the weight of the long handle, under-greasing brings in its train a considerable amount of friction and a corresponding diminution in the benefit derived from the long handle. Further the beginner generally does not know the right amount of pressure to be applied to the tip of the handle for effecting a certain desired rotation of the barrel with

the result that the gas velocity is not completely under his control. The use of the simple device described in this paper while being considerably helpful even to the expert micro-analyst, makes the determination safe even in the hands of the beginner.

Figs. 1 and 2 give the plan and the elevation of the device which consists of an ebonite piece carrying two screws, while Figs. 3 and 4 represent the same when it is fixed on to the connecting piece. The non-tapering portion of the connecting piece can easily pass through the hole (A) and the ebonite piece fixed rigidly at any desired position on the glass part by means of the screw (B) which controls the cleft shown. The screw (C) controls the movement of the stop-cock, every forward movement tending to close the



Scale 1″= 1½″.

channel in the stop-cock while every backward movement has the opposite effect. The ebonite piece is fixed at such a position that the stop-cock is completely closed when the screw can advance no farther. By gradually working it backwards the stop-cock is gently opened by the action of the elastic band (D) and it is possible by turning the milled head of the screw by about 5 or 10° at a time to get any gas speed required. Whenever during the

course of the experiment it is necessary to have the long handle parallel to the body of the connecting piece so as to get a straight passage for the gas, the band can be slipped off and the handle taken to any desired position.

The device has been tested in a number of estimations and found very satisfactory. It is easily fixed to the connecting piece and any desired gas speed obtained and maintained without any difficulty. There is no strain on any part of the apparatus because of the shape of the ebonite piece the weight of which is small. The part is easy to construct and costs little. It was made in the Instruments Section of this University.

The author's thanks are due to Dr. G. Gangadharam for the drawings.

GENERALIZATION OF A THEOREM OF DICKSON.

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1. Dickson[1] showed that the congruence

$$x^k + y^k + 1 \equiv 0 \pmod{p}$$

always has a solution with $xy \not\equiv 0 \pmod{p}$

$$\text{if } p \geqslant (k-1)^2 (k-2)^2 + 6k - 2,$$

where k and p are odd primes.

In this paper I give a simple proof, by a different method based on lemmas due to Hardy and Littlewood, of this result in the generalized form :

Theorem : *Let* p *denote a prime and let* n *be prime to* p, *then the number* N, *of solutions of*

$$x^k + y^k \equiv n \pmod{p}$$

$$1 \leqslant x \leqslant p, \quad 1 \leqslant y \leqslant p, \quad xy \not\equiv 0 \pmod{p}$$

satisfies

$$N \geqslant p - (k-1)(k-2)\sqrt{p} - (3k-1)$$

and hence there is always a solution, if

$$p \geqslant (k-1)^2 (k-2)^2 + 6k - 2$$

provided $k \geqslant 6$.

It is curious that the lower limit for p obtained by our method is exactly the same as that obtained by Dickson. Incidentally we give a new proof of a recent result due to Davenport and Hasse.[2]

2. *Notation.* In this section k is any fixed integer ≥ 6.

$S_\rho = \sum_{h=1}^{q} \rho^{h^k}$ where ρ is a primitive qth root of unity, *i.e.*, $\rho = e^{2\pi i a/q}$ where $(a, q) = 1$.

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[1] *Jour für Math.*, 135, (1909), 181–88.

See also A. Hurnitz (*Journal für Mathematik*, **136**, (1909), pp. 272–92, who also generalizes the theorem in question by other methods.

[2] *Crelle's Journal*, **172**, (1934), 151–82. The equation (1) below is also proved in their paper.

$A(q) = A(q, n) = q^{-2} \Sigma_\rho (S_\rho)^2 \rho^{-n}$ where ρ runs over the $\phi(q)$ primitive qth roots of unity.

$M(p, n)$ is the number of solutions of $h_1^k + h_2^k \equiv n \pmod p$ where $0 \leqslant h_1 < p$, $0 \leqslant h_2 < p$.

Lemma 1.[3]

$$1 + A(p) = p^{-1} M(p, n).$$

Lemma 2. *If* $\rho \neq n$,

$$|A(p)| \leqslant \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}$$

Proof. Write $\epsilon = e^{2\pi i/p}$, and for each character $\chi \pmod p$

$$\tau_\chi = \sum_{l=1}^{p-1} \epsilon^l \chi(l) = \sum_l \epsilon^l \chi(l)$$

We have (LV, satz 308)

$\tau_{\chi_0} = -1$ (where χ_0 is the principal character) $|\tau_\chi| = \sqrt{p}$ $(\chi \neq \chi_0)$.

The $\delta = (k, p-1)$ characters χ with the property that $\chi^k = \chi_0$ (LV, satz 309) are called " special characters " and will be denoted by the letter ψ, $\psi_0 = \chi_0$.

We have (LV, satz 310) when

$$q = p, \quad \rho = \epsilon^r, \quad \text{where } (r, p) = 1,$$

$$S_\rho = \sum_{\psi \neq \psi_0} \psi(r)\, \tau_{\bar\psi}$$

We have also (LV, satz 317).

$$A(p) = p^{-2} \sum_{\psi_1, \psi_2} \tau_{\psi_1} \tau_{\psi_2} \sum_{r=1}^{p-1} l^{\frac{-2\pi i r n}{p}} \bar\psi_1(r)\, \bar\psi_2(r)$$

$$= p^{-2} \{ \sum'_{\psi_1, \psi_2} (\ ) + \sum''_{\psi_1, \psi_2} (\ ) \}$$

[where ψ_1, ψ_2 run independently over the $(\delta - 1)$ special characters $\psi \neq \psi_0$] and in Σ' the summation is for ψ_1, ψ_2 subject to $\bar\psi_1 \bar\psi_2 \neq \chi_0$ and in Σ'' the ψ_1, ψ_2 satisfy $\bar\psi_1 \psi_2 = \chi_0$. The number of terms in $\sum_{\psi_1, \psi_2}$ is $(\delta - 1)^2$. The number of terms in $\sum''_{\psi_1, \psi_2}$ is $\delta - 1$ and hence in $\sum'_{\psi_1, \psi_2}$ there are $(\delta - 1)$, $(\delta - 2)$ terms. Now we have

$$|\tau_{\psi_1} \tau_{\psi_2}| = p.$$

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[3] E. Landau, *Vorlesungenüber Zahlentheorie*, 1, satz 286. We refer to this book as LV.

The inner sum is, since every time $\bar{\psi}_1(r)\,\psi_2(r)$ is a character $\chi(r)$ [and without loss of generality $0 < n < p$]

$$= \sum_{r=1}^{p-1} \epsilon^{-rn}\chi(r) = \sum_{r=1}^{p-1} \epsilon^{r(p-n)}\chi(r)$$

$$= \bar{\chi}(p-n) \sum_{r=1}^{p-1} \epsilon^{r(p-n)}\chi[r(p-n)]$$

$$= \bar{\chi}(p-n) \sum_{r=1}^{p-1} \epsilon^{r}\chi(r) = \bar{\chi}(p-n)\,\tau_\chi$$

Hence

$$|\Sigma| \leqslant |\Sigma'| + |\Sigma''| \leqslant (\delta-1)(\delta-2)(p\sqrt{p} + (\delta-1)p.1.$$

whence

$$|A(p)| \leqslant \frac{(\delta-1)(\delta-2)}{\sqrt{p}} + \frac{\delta-1}{p} \leqslant \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}.$$

3. *Concluding argument.* We observe that from lemmas 1 and 2

$$|p^{-1}M(p,n) - 1| \leqslant \frac{(k-1)(k-2)}{\sqrt{p}} + \frac{k-1}{p}$$

whence

(1) $M(p,n) \geqslant p - (k-1)(k-2)\sqrt{p} - (k-1).$

It is easily seen that

$$N \geqslant M(p,n) - 2k \geqslant p - (k-1)(k-2)\sqrt{p} - (k-1) - 2k$$
$$= p - (k-1)(k-2)\sqrt{p} - (3k-1)$$

and therefore $N > 0$ if

$$\sqrt{p} > \alpha = \frac{(k-1)(k-2) + \sqrt{(k-1)^2(k-2)^2 + 4(3k-1)}}{2}$$

where α is the larger root of

$$x^2 - (k-1)(k-2)x - (3k-1) = 0.$$

Now,

$$\alpha = (k-1)(k-2)\left\{\tfrac{1}{2} + \tfrac{1}{2}\sqrt{1 + \frac{4(3k-1)}{(k-1)^2(k-2)^2}}\right\}$$

$$< (k-1)(k-2)\left\{\tfrac{1}{2} + \tfrac{1}{2}\left(1 + \tfrac{1}{2}\cdot\frac{4(3k-1)}{(k-1)^2(k-2)^2}\right)\right\}$$

since $\sqrt{1+z} < 1 + \frac{1}{2}z$ for $z > 0$. Thus

$$\alpha < (k-1)(k-2) + \frac{3k-1}{(k-1)(k-2)}$$

$$\alpha^2 < (k-1)^2(k-2)^2 + 2(3k-1) + \left\{\frac{3k-1}{(k-1)(k-2)}\right\}^2$$

Hence $N > 0$ if

$$p \geqslant (k-1)^2 (k-2)^2 + 6k - 2 + \left\{\frac{3k-1}{(k-1)(k-2)}\right\}^2$$

i.e., if

(2) $\quad p > (k-1)^2 (k-2)^2 + 6k - 2$

since

$$\frac{3k-1}{(k-1)(k-2)} < 1 \quad \text{for } k \geqslant 7.$$

But since the right-hand side of (2) is a multiple of 2, (2) is equivalent to (3) $p \geqslant (k-1)^2 (k-2)^2 6k - 2$. Thus $N > 0$ if p satisfies (3) and our theorem is proved.

NOTE ON HARMONIC FUNCTIONS.

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§1. *Introduction.*

According to a well-known theorem of Gauss, every function u regular and harmonic in a region G possesses, for every sphere S—centre P (x, y, z) and radius R—lying entirely inside G, the mean value property:

$$\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q = u\,(P) \tag{1}$$

The converse of this theorem, that if u is continuous and possesses the property (1) for every sphere in G then u is harmonic in G, was discovered by Bôcher and Koebe. In other words, the property (1) is a characteristic one for functions harmonic in G. A number of conditions each of which characterises a harmonic function have since been given. For instance Zaremba[1] proved that if

$$\lim_{h\to 0}\frac{1}{h^2}\left[\sum_{x\,y\,z}\{u\,(x+h,y,z)+u\,(x-h,y,z)\}-6\,u\,(x\,y\,z)\right]=0$$

then $\nabla^2 u = 0$. The condition (1) was generalised by Blaschke[2] and may be stated as follows: A necessary and sufficient condition that the continuous function u be harmonic in G is

$$\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q - u\,(P)\right]=0 \tag{2}$$

for every sphere S in G. Results similar to those of Zaremba and Blaschke have been recently obtained by Kappos.[3] Saks[4] has used Blaschke's theorem to derive two other properties either of which may be regarded as the defining property of harmonic functions. In this paper it will be shown that results analogous to those of Blaschke and Saks may be obtained for solutions of Poisson's equation and also of the equation $\nabla^2 u + cu = 0$. The following results are obtained:

(I) If $\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,dS - u\,(P) + \iiint_K\left(\frac{1}{r}-\frac{1}{R}\right)\mu\,d\tau\right]=0,$

then $\nabla^2 u + 4\pi\mu = 0.$

(II) If $\lim_{R\to 0} \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,dS - u(P)\frac{f(R)}{f(0)}\right] = 0,$

then $\nabla^2 u - \frac{3f''(0)}{f(0)}\,u = 0.$

The first reduces to Blaschke's theorem for $\mu = 0$ and the second is the converse of a mean-value theorem due to Weber.[5] Making the same use of theorems I and II as Saks has done of Blaschke's theorem, the following further results are obtained :

(III) If $\lim_{R\to 0} \frac{1}{2R}\left[\frac{1}{4\pi}\iint_S \frac{\partial u}{\partial R}\,d\Omega + \frac{1}{R^2}\iiint_K \mu\,d\tau\right] = 0,$

then $\nabla^2 u + 4\pi\mu = 0.$

(IV) Let $\nabla^2 v = 0$ and $v \neq 0$. Then, if

$$\lim_{R\to 0} \frac{1}{R^3}\left[\frac{1}{4\pi}\iint_S \left(v\frac{\partial u}{\partial R} - u\frac{\partial v}{\partial R}\right) dS + \iiint_K v\mu\,d\tau\right] = 0,$$

$\nabla^2 u + 4\pi\mu = 0.$

(V) If $\lim_{R\to 0} \frac{1}{4\pi R}\iint_S \frac{\partial u}{\partial R}\,d\Omega = cu(P)$, then $\nabla^2 u - 3cu = 0.$

The theorems III and IV correspond to those of Saks, to which they reduce when $\mu = 0$. The restrictions imposed on the functions u, μ, f in these theorems are mentioned below, in the proper contexts.

§2. *A Lemma.*

Let P (x, y, z) be an interior point of G and let the function $\psi(x, y, z, r) = \psi(P; r)$ satisfy the conditions : (i) $\psi(x, y, z, r)$ is continuous in all its arguments, and (ii) $\lim_{r\to 0} \psi(x, y, z, r) = 0$. Then if

$$J(P) = \frac{1}{a^3}\int_0^a r^4\,\psi(P; r)\,dr$$

we have

$$\lim_{P'\to P} \frac{J(P') - J(P)}{P'P} = 0 \qquad (2\cdot1)$$

In fact we may choose axes so that PP′ is parallel to the z-axis. Let $(x, y, z + h)$ be the co-ordinates of P′. Then

$$\frac{J(P') - J(P)}{P'P} = \frac{1}{a^3}\int_0^a \frac{\psi(P'; r) - \psi(P; r)}{h}\,r^4\,dr$$

Since $\psi(P; r) \to 0$ as $r \to 0$ we can find r_0 such that $|\psi(P; r)| < \frac{h^2}{2}$ for $r < r_0$; and since $\psi(P; r) = \psi(x, y, z, r)$ is continuous in all its arguments

this continuity will be uniform. Then r_0 will depend upon h only, $r_0 \equiv r_0(h)$, and the above inequality will hold also for $\psi(P'; r)$ with the same r_0. Since the upper limit a in J (P) is arbitrary we may choose it so that $a < r_0(h)$. We then have

$$\left|\frac{J(P') - J(P)}{P'P}\right| = \left|\frac{1}{a^3}\int_0^a \frac{\psi(P'; r) - \psi(P; r)}{h} r^4\, dr\right|$$

$$< \frac{h}{a^3}\int_0^a r^4\, dr = \frac{1}{5}ha^2$$

from which it is evident that $\lim_{P' \to P} \frac{J(P') - J(P)}{P'P} = 0.$

This proves the lemma. I am not aware of the proof given by Blaschke of his theorem, but it must be noticed that his theorem is an immediate consequence of our lemma. For writing

$$\psi(P; R) = \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P)\right]$$

so that if u is continuous, ψ satisfies the conditions of the lemma.

We then have $u(P) = \frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - R^2\psi(P; R)$

and integrating from 0 to a w.r.t R, we get

$$u(P) = \frac{3}{4\pi a^3}\iiint_K u\, d\tau - \frac{3}{a^3}\int_0^a R^4\, \psi(P; R)\, dR$$

[K is the volume inside a sphere of rad. a and centre P.]

$$= I(P) - J(P).$$

To calculate $\frac{\partial u_P}{\partial z}$, for instance, we take $P'(x, y, z + h)$ and compute the limit $\lim_{h \to 0} \frac{u(P') - u(P)}{h}$. The lemma shows that J (P) disappears in this process and we have

$$\frac{\partial u}{\partial z} = \lim_{h \to 0} \frac{I(P') - I(P)}{h}.$$

From this point onwards the argument runs on the usual lines[6] and we infer the existence and continuity of the second derivatives of u. We now have by Green's theorem

$$\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P) = \frac{1}{4\pi}\iiint_K \left(\frac{1}{r} - \frac{1}{R}\right)\nabla^2 u\, d\tau,$$

where r = distance of $d\tau$ from P, the centre of the sphere.

$$\therefore \lim_{R\to 0} \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q - u\,(P)\right]$$

$$= \lim_{R\to 0} \frac{1}{4\pi R^2}\iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\nabla^2 u\,d\tau$$

$$= (\nabla^2 u)_P \cdot \lim_{R\to 0}\frac{1}{4\pi R^2}\iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)d\tau$$

$$= \frac{1}{6}(\nabla^2 u)_P.$$

Since the value of the left-hand side is zero, it follows that $\nabla^2 u = 0$. This proves the sufficiency of the condition. Since by Gauss's theorem the condition is evidently necessary, we have herewith proved Blaschke's theorem.

§3. *Poisson's Equation.*

Let μ be a given function continuously differentiable in G. Let u be continuous in G and let it satisfy further, for every sphere in G, the condition

$$\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q - u\,(P) + \iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\mu\,d\tau\right] = 0 \quad (3\cdot 1)$$

Put

$$\psi\,(P\,;R) = \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q - u\,(P) + \iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\mu\,d\tau\right]$$

so that

$$u\,(P) = \frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q + \iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\mu\,d\tau - R^2\psi\,(P\,;R).$$

Multiplying by R^2 and integrating from 0 to R w.r.t. R, this gives

$$u\,(P) = \frac{3}{4\pi R^3}\iiint_K u\,d\tau + \iiint_K \frac{(R-r)^2\,(2R+r)}{2rR^3}\,\mu\,d\tau$$

$$- \frac{3}{R^3}\int_0^R R^4\,\psi\,(P\,;R)\,dR$$

$$= I\,(P) + L\,(P) - J\,(P).$$

Taking P′ to be the point $(x,\ y,\ z+h)$, we compute as before $\frac{\partial u_P}{\partial z} = \lim_{h\to 0}\frac{u\,(P') - u\,(P)}{h}$. In this process the integral J (P) will disappear by the Lemma. If μ is continuously differentiable, then $\mu_1 = \frac{(R-r)^2\,(2R+r)}{2R^3}\,\mu$ is also continuous and continuously differentiable and by a well-known

theorem in Potential Theory L (P) $= \iiint_K \frac{\mu_1}{r}\, d\tau$ possesses continuous second derivatives. We may now apply the usual type of reasoning to I (P) and infer the existence of continuous second derivatives for I (P). Thus we conclude that under the given condition u is twice continuoulsy differentiable. But if this is so we have

$$\lim_{R\to 0} \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\, dS_Q - u\,(P)\right]$$

$$= \lim_{R\to 0} \frac{1}{R^2}\,\frac{1}{4\pi}\iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\nabla^2 u\, d\tau$$

$$= (\nabla^2 u)_P \lim_{R\to 0}\frac{1}{4\pi R^2}\iiint_K \left(\frac{1}{r}-\frac{1}{R}\right) d\tau$$

$$= \frac{1}{6}(\nabla^2 u)_P$$

while

$$\lim_{R\to 0}\frac{1}{R^2}\iiint\left(\frac{1}{r}-\frac{1}{R}\right)\mu d\tau = \mu_P \cdot \lim_{R\to 0}\frac{1}{R^2}\iiint_K\left(\frac{1}{r}-\frac{1}{R}\right) d\tau$$

$$= \frac{4\pi}{6}\mu_P.$$

Hence the given condition is equivalent to

$$\nabla^2 u + 4\pi\mu = 0.$$

We have thus the result:

If u *is continuous in* G *and satisfies the condition* (3·1) *for every sphere in* G, *then* $\nabla^2 u + 4\pi\mu = 0$.

For $\mu = 0$, this reduces to Blaschke's theorem. The condition (3·1) will be satisfied in particular if for every sphere in G

$$u\,(P) = \frac{1}{4\pi R^2}\iint_S u\,(Q)\, dS_Q + \iiint_K \left(\frac{1}{r}-\frac{1}{R}\right)\mu d\tau \qquad (3\cdot 2)$$

Thus if the continuous function u satisfies the condition (3·2) for every sphere in G, then u satisfies Poisson's equation at every point of G. This is an extension to Poisson's equation of the converse theorem of Bocher and Koebe, and is well known.[7]

§4. *Pockels' Equation.*

Next consider the equation $\nabla^2 u + cu = 0$. Every regular solution of this equation satisfies the mean-value property

$$\frac{1}{4\pi R^2}\iint_S u\,(Q)\, dS_Q = u\,(P)\cdot\frac{\sin R\sqrt{c}}{R\sqrt{c}} \qquad (4\cdot 1)$$

a result due to Weber. We may prove a converse theorem in this case, similar to that of Blaschke. Let $f(x)$ be twice continuously differentiable, with $f(0)$ finite, $\neq 0$, and $f'(0) = 0$. Let the continuous function u satisfy the condition

$$\lim_{R \to 0} \psi(P ; R) = 0$$

where

$$\psi(P ; R) = \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P)\,\frac{f(R)}{f(0)}\right]$$

We then have

$$\frac{f(R)}{f(0)}\, u(P) = \frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - R^2 \psi(P ; R)$$

Multiplying by R^2 and integrating from 0 to a w.r.t. R we get

$$C\, u(P) = \frac{1}{4\pi}\iiint_K u\, d\tau - \int_0^a R^4 \psi(P ; R)\, dR$$

with

$$C = \int_0^a \frac{f(R)}{f(0)}\, R^2\, dR.$$

By reasoning exactly as before we conclude that $u(P)$ is twice continuously differentiable.

Now

$$\frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P)\,\frac{f(R)}{f(0)}\right]$$

$$= \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P)\right] - \frac{u(P)}{f(0)} \cdot \frac{f(R) - f(0)}{R^2}$$

Since u is twice continuously differentiable

$$\lim_{R \to 0} \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u(Q)\, dS_Q - u(P)\right] = \frac{1}{6}(\nabla^2 u)_P ;$$

and

$$\lim_{R \to 0} \frac{f(R) - f(0)}{R^2} = \frac{1}{2} f''(0)$$

Thus the assumed condition leads to $\nabla^2 u - \dfrac{3f''(0)}{f(0)}\, u = 0$. We have thus obtained the following result :

If u *be continuous in* G *and if for every sphere in* G

$$\lim_{R\to 0} \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q - u\,(P)\,\frac{f\,(R)}{f\,(0)}\right] = 0 \qquad (4\cdot 2)$$

then $\nabla^2 u + cu = 0$ *with* $c = -3\,f''\,(0)/f\,(0)$, provided that $f\,(x)$ satisfies the conditions specified above.

In particular if $f''\,(0) = 0$, then u must be harmonic. The condition (4·2) will be satisfied if for every sphere in G

$$\frac{1}{4\pi R^2}\iint_S u\,(Q)\,dS_Q = u\,(P)\,\frac{f\,(R)}{f\,(0)}.$$

Taking $f\,(x) = \dfrac{\sin\sqrt{c}.\,x}{\sqrt{c}.\,x}$ we obtain the converse of Weber's mean-value theorem.

§5. *Generalisations to* n *Dimensions.*

These results may immediately be generalised to n dimensions. Thus taking the case of Poisson's equation, the corresponding result will here be as follows: Let u be continuous in G and let it satisfy for every sphere Ω_R, centre P and radius R, in G, the condition

$$\lim_{R\to 0} \frac{1}{R^2}\left[\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,(Q)\,d\Omega - u\,(P) + \frac{1}{n-2}\iint\cdots\int_{K_R}\left(\frac{1}{r^{n-2}} - \frac{1}{R^{n-2}}\right)\mu\,d\tau\right] = 0 \qquad (5\cdot 1)$$

where K_R is the volume inside Ω_R, μ is a continuously differentiable function, and ω_n is the surface-area of the unit sphere in n dimensions. Then u is twice continuously differentiable and satisfies in G the equation

$$\nabla^2 u + \omega_n \mu = 0$$

where now

$$\nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \cdots + \frac{\partial^2}{\partial x_n^2}.$$

In fact the proof of the differentiability of u proceeds exactly as before and then we have, by the corresponding form of Green's theorem in n dimensions,

$$\frac{1}{R^2}\left[\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,d\Omega - u\,(P)\right] = \frac{1}{\omega_n (n-2)}\cdot\frac{1}{R^2}\iint\cdots\int_{K_R}\left(\frac{1}{r^{n-2}} - \frac{1}{R^{n-2}}\right)\nabla^2 u\,d\tau$$

so that

$$\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,d\Omega - u(P)\right]$$

$$=\frac{(\nabla^2 u)_P}{\omega_n (n-2)}\lim_{R\to 0}\frac{1}{R^2}\iint\cdots\int_{K_R}\left(\frac{1}{r^{n-2}}-\frac{1}{R^{n-2}}\right)d\tau$$

$$=\frac{(\nabla^2 u)_P}{\omega_n (n-2)}\lim_{R\to 0}\frac{1}{R^2}\int_0^R\left(\frac{1}{r^{n-2}}-\frac{1}{R^{n-2}}\right)\omega_n r^{n-1}\,dr$$

$$=\frac{1}{2n}(\nabla^2 u)_P$$

and $$\lim_{R\to 0}\frac{1}{R^2}\cdot\frac{1}{n-2}\iint\cdots\int_{K_R}\left(\frac{1}{r^{n-2}}-\frac{1}{R^{n-2}}\right)\mu d\tau=\frac{\omega_n}{2n}\mu_P$$

Thus u satisfies the equation $\nabla^2 u+\omega_n\mu=0$.

Again let u be continuous in G and satisfy the condition

$$\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,d\Omega - u(P)\frac{f(R)}{f(0)}\right]=0 \qquad (5\cdot 2)$$

$f(x)$ being such that $f(0)\neq 0, f'(0)=0, f''(x)$ continuous. Then u satisfies the equation

$$\nabla^2 u-\frac{nf''(0)}{f(0)}u=0.$$

For the differentiability of u being proved exactly as before we have

$$\lim_{R\to 0}\frac{1}{R^2}\left[\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,d\Omega - u(P)\right]\frac{u(P)}{f(0)}\lim_{R\to 0}\frac{f(R)-f(0)}{R^2}$$

i.e.,
$$\frac{1}{2n}(\nabla^2 u)_P=\tfrac{1}{2}\frac{f''(0)}{f(0)}u_P$$

or

$$\nabla^2 u-\frac{nf''(0)}{f(0)}u=0 \qquad (5\cdot 3)$$

The result will be true in particular if we replace the condition (5·2) by

$$\frac{1}{\omega_n R^{n-1}}\int\cdots\int_{\Omega_R} u\,d\Omega = u(P)\cdot\frac{f(R)}{f(0)} \qquad (5\cdot 4)$$

This result that under the condition (5·4) u satisfies the equation (5·3) has been proved as a particular case of a more general theorem and in a different way by H. Poritsky in a recent paper.[8]

§6. *Analogues of Saks's Theorems.*

Consider first the case of Poisson's equation. Then the analogues of Saks's theorems to this case may be stated as follows :

(i) *Let* u *be continuous, with its first partial derivatives, in* G *and let it satisfy for every sphere in* G *the condition*

$$\lim_{R\to 0} \frac{1}{2R}\left[\frac{1}{4\pi}\int\int_S \frac{\partial u}{\partial R}\,d\Omega + \frac{1}{R^2}\int\int\int_K \mu\,d\tau\right] = 0 \qquad (6\cdot 1)$$

where μ *is continuously differentiable. Then* $\nabla^2 u + 4\pi\mu = 0$. (Here $d\Omega$ means the element of area on the unit sphere.)

(ii) *Let* $\nabla^2 v = 0$, $v \neq 0$, *in* G. *If* u *be continuous, with its partial derivatives, in* G *and satisfies for every sphere in* G *the condition*

$$\lim_{R\to 0} \frac{1}{R^3}\left[\frac{1}{4\pi}\int\int_S \left(v\frac{\partial u}{\partial R} - u\frac{\partial v}{\partial R}\right)dS + \int\int\int_K v\mu\,d\tau\right] = 0 \qquad (6\cdot 2)$$

then u *satisfies* $\nabla^2 u + 4\pi\mu = 0$.

The method of proof is identical with that used by Saks, except that whereas Saks makes use of Blaschke's theorem, we here use the analogue of Blaschke's theorem proved in § 3 above, from which the first theorem is an immediate consequence. Following an ingenious procedure due to Saks we may write

$$\psi(R) = \frac{1}{R^2}\left[\frac{1}{4\pi R^2}\int\int_S u\,dS - u(P) + \int\int\int_K \left(\frac{1}{r} - \frac{1}{R}\right)\mu\,d\tau\right]$$

and apply l'Hospital's rule of the differential calculus to find $\lim_{R\to 0}\psi(R)$. This procedure gives

$$\lim_{R\to 0}\psi(R) = \lim_{R\to 0}\frac{1}{2R}\frac{d}{dR}\left[\frac{1}{4\pi R^2}\int\int_S u\,dS - u(P) + \int\int\int_K \left(\frac{1}{r} - \frac{1}{R}\right)\mu\,d\tau\right]$$

$$= \lim_{R\to 0}\frac{1}{2R}\left[\frac{1}{4\pi}\int\int_S \frac{\partial u}{\partial R}\,d\Omega + \frac{1}{R^2}\int\int\int_K \mu\,d\tau\right].$$

If therefore the right-hand limit vanishes, so does $\lim_{R\to 0}\psi(R)$ and hence by the theorem of § 3, u satisfies $\nabla^2 u + 4\pi\mu = 0$. This proves theorem (i). The second theorem now follows from the first, exactly as in Saks's paper. Finally consider the analogue of Saks's theorem with respect to the equation $\nabla^2 u + cu = 0$. Let u be continuous, with its first partial derivatives, in G

and let $f(x)$ satisfy the conditions specified in § 4. If we now write

$$\psi(R) = \frac{1}{R^2}\left[\frac{1}{4\pi}\int\int_S u\, d\Omega - u(P)\,\frac{f(R)}{f(0)}\right]$$

we find as above

$$\lim_{R\to 0}\psi(R) = \lim_{R\to 0}\frac{1}{2R}\left[\frac{1}{4\pi}\int\int_S \frac{\partial u}{\partial R}\, d\Omega - u(P)\,\frac{f'(R)}{f(0)}\right]$$

Under the hypotheses regarding $f(x)$ we have

$$\lim_{R\to 0}\frac{f'(R)}{R} = \lim_{R\to 0}\frac{f'(R)-f'(0)}{R} = f''(0).$$

We thus find that if

$$\lim_{R\to 0}\left[\frac{1}{4\pi R}\int\int_S \frac{\partial u}{\partial R}\, d\Omega - u(P)\,\frac{f''(0)}{f(0)}\right] = 0$$

then $\lim_{R\to 0}\psi(R) = 0$ and hence by § 4, u satisfies $\nabla^2 u - \frac{3f''(0)}{f(0)}u = 0$. Writing $c = \frac{f''(0)}{f(0)}$, this result may be stated as follows:

If u *be continuous, with its first partial derivatives, in* G *and satisfies for every sphere in* G *the condition*

$$\lim_{R\to 0}\frac{1}{4\pi R}\int\int_S \frac{\partial u}{\partial R}\, d\Omega = cu(P) \qquad (6\cdot 3)$$

then u *satisfies at every point of* G *the equation*

$$\nabla^2 u - 3c\,u = 0.$$

In conclusion, I wish to acknowledge my indebtedness to Prof. B. S. Madhava Rao for drawing my attention to the problem and for kind guidance.

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A REMARK ON g (*n*).

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Pillai* proved that, for $n > n_0$,

$$g(n) = 2^n + \left[\left(\frac{3}{2}\right)^n\right] - 2 \tag{1}$$

provided

$$3^n = l \cdot 2^n + r \ (0 < r < 2^n) \text{ where } r \geqslant 2^n - (l+3).$$

By combining this with a recent theorem of Mahler (*Acta arithmetica*, Band 3, p. 93, Theorem 4) we obtain the result

Theorem : *Let A be an arbitrarily large number. Then there exist infinitely many* x *such that* (1) *is true for* $x \leqslant n \leqslant Ax$.

Another form is the following :

Theorem : *Let* ϵ *be an arbitrarily small positive number, then there exist infinitely many* x *such that the number of values of* n *for which* $2 \leqslant n \leqslant x$ *and in addition* (1) *is true, is less than* ϵx.

(All letters, except ϵ, denote positive integers.)

In fact if we denote by K (*x*), the number of solutions of

$$\left.\begin{matrix} 1 \leqslant n \leqslant x \\ g(n) = 2^n + \left[\left(\frac{3}{2}\right)^n\right] - 2 \end{matrix}\right\},$$

the above results can be put elegantly in the following form :

Theorem :

$$\lim_{x \to \infty} \sup \frac{K(x)}{x} = 1$$

Pillai proved that

$$\frac{K(x)}{x} > \frac{1}{4} \ (x > x_0).$$

* *Annamalai University Journal*, March 1936, 5, No. 2. The result mentioned was also proved by Dickson.

ON AN INFINITE SYSTEM OF NON-LINEAR INTEGRAL EQUATIONS.

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1. The aim of this note is to solve the infinite system of Non-Linear Integral equations

$$y_n(x) = \int_0^x K_n(x,t)\, F_n(t, y_1(t), y_2(t) \cdots)\, dt \qquad (1)$$

$$n = 1, 2, 3, \cdots$$

so that the functions $[y_n(t)]$ may belong to Hilbert Space that is to say, the series $\sum_{n:1}^{\infty} [y_n(t)]^2$ may be convergent uniformly for all values of t in a definite interval. If the functions $F_n(t; x_1 x_2 \cdots)$ are all analytic in the infinity of variables $x_1, x_2, \cdots$ and continuous with respect to the variable t, we can solve the system (1) so that $\sum_{n:1}^{\infty} y_n(t)$ is absolutely and uniformly convergent, with suitable hypothesis. The general theory of such equations had been developed by Dr. M. R. Siddiqi in a series of extension lectures given by him to the Lucknow University in January 1938, which are being published. But it is shown here that we can solve (1) uniquely with the more general hypothesis that the functions F_n are uniformly continuous with respect to all the variables and satisfy Lipschitz condition. The solution is got by method of successive approximations.

2. Our attempt is to solve the system (1), where x lies in the interval $0 \leqslant x \leqslant T$, such that for all values of x in the interval, the series

$$\sum_{n:1}^{\infty} [y_n(x)]^2 \qquad (2)$$

may be uniformly convergent. We assume that the functions $F_n(t; x_1, x_2 \cdots)$ are, for all values of t in the interval and all real values of $x_1, x_2, \cdots$ belonging to Hilbert Space, continuous and satisfy Lipschitz's condition

$$[F_n(t; x_1, x_2, \cdots) - F_n(t; x_1', x_2', \cdots)]^2 \leqslant l_n^2 \sum_{i:1}^{\infty} (x_i - x_i')^2 \qquad (3)$$

where l_n is a positive constant, such that

$$\sum_{n=1}^{\infty} l_n^2 \int_0^x [K_n(x,t)]^2\, dt < a \tag{4}$$

where 'a' is a constant independent of x. We further assume

$$F_n(t;0;0,\cdots) \not\equiv 0 \quad n: 1, 2, \cdots \tag{5}$$

$$\sum_{n:1}^{\infty} \left(\int_0^x K_n(x,t)\, F_n(t;0,\cdots)\, dt \right)^2 < b \tag{6}$$

where b is a constant independent of x:

We now solve the system (1) by the method of successive approximations. For this purpose, we write

$$\begin{cases} y_n^0 = 0 \\ y_n^m(x) = \int_0^x K_n(x,t)\, F_n[t; y_1^{m-1}(t), y_2^{m-1}(t), \cdots]\, dt \end{cases} \tag{7}$$

$$m: 1, 2 \cdots$$

We prove that the systems (y_n^m) approximate to (y_n) so that

$$\lim_{m\to\infty} \sum_{n:1}^{\infty} (y_n^m)^2 = \sum_{n:1}^{\infty} (y_n^m)^2 \tag{8}$$

and thus solve (1) completely. We write

$$\begin{cases} \chi_m^2(x) = \sum_{n:1}^{\infty} (y_n^m - y_n^{m-1})^2 \\ \chi_1^2(x) = \sum_{n:1}^{\infty} (y_n^1)^2 < b. \end{cases} \tag{9}$$

Now from (7)

$$y_n^{m+1} - y_n^m = \int_0^x K_n(x,t)\,[F_n(t; y_1^m(t), y_2^m(t)\cdots) - F_n(t; y_1^{m-1}(t)\cdots)]\, d$$

and so

$$(y_n^{m+1} - y_n^m)^2 \leqslant l_n^2 \int_0^x [K_n(x,t)]^2 \cdot dt \cdot \int_0^x \chi_m^2(t)\, dt \tag{10}$$

on account of Schwarz's inequality and (3). Summing from $n = 1$ to ∞ we observe

$$\begin{aligned} \chi_{m+1}^2(x) &\leqslant a \int_0^x \chi_m^2(t)\, dt \\ &\leqslant \frac{a^{m+1}}{\Gamma(m+1)} \int_0^x (x-t)^m \chi_1^2(t)\, dt \\ &\leqslant \frac{b\, a^{m+1} x^{m+1}}{\Gamma(m+2)} \end{aligned} \tag{11}$$

by induction and by (9). From (10) and (11) we at once observe that $\sum_{m:0}^{\infty} (y_n^{m+1} - y_n^m)$ is absolutely and uniformly convergent in (0 T), so that,

$$\lim_{m \to \infty} y_n^m = y_n \tag{12}$$

exists uniformly for all x in (0 T). To prove that the systems (y_n^m) and (y_n) belong to Hilbert Space, we observe as in (10) and (11)

$$\sum_{n:1}^{\infty} (y_n^{m+1} - y_n^1)^2 \leqslant a \int_0^x \sum_{n:1}^{\infty} [y_n^m(t)]^2 \, dt \tag{13}$$

Now
$$\sum_{n:1}^{\infty} (y_n^{m+1})^2 = \sum_{n:1}^{\infty} [y_n^1 + (y_n^{m+1} - y_n^1)]^2$$
$$\leqslant 2 \Sigma (y_n^1)^2 + 2 \Sigma (y_n^{m+1} - y_n^1)^2$$

and so

$$\sum_{n:1}^{\infty} [y_n^{m+1}(x)]^2 \leqslant 2b + 2a \int_0^x \sum_{n:1}^{\infty} [y_n^m(t)^2] \, dt. \tag{14}$$

Here also by induction we have

$$\sum_{n:1}^{\infty} [y_n^{m+1}(x)]^2 \leqslant 2b + 2^2 b\, ax + \cdots + \frac{2^{m+1} b a^m x^m}{m!}$$
$$< 2b\, e^{2ax} \tag{15}$$

(15) clearly shows that $\sum_{n:1}^{\infty} (y_n^{m+1})^2$ is uniformly bounded for all values of x in (0 T) and all values of m. Therefore $\sum_{n:1}^{\infty} y_n^2$ is convergent for all values of x in (0 T)

To prove (8) we put

$${}_p\mathrm{R}_m(x) = \sum_{n:1}^{\infty} (y_n^{m+p} - y_n^m)^2 \tag{16}$$

and observe as in (11)

$${}_p\mathrm{R}_m(x) \leqslant a \int_0^x {}_p\mathrm{R}_{m-1}(t) \, dt \tag{17}$$
$$\leqslant \frac{a^m}{\Gamma(m)} \int_0^x (x - t)^{m-1} \, {}_p\mathrm{R}_0(t) \, dt$$

Now from (15),

$${}_p\mathrm{R}_0(x) = \sum_{n:1}^{\infty} [y_n^p(x)]^2 \leqslant 2b\, e^{2ax} \tag{18}$$

and therefore (17) shows that

$$(19) \qquad {}_p\mathrm{R}_m \leqslant \frac{2ba^m}{\Gamma(m)} \int_0^x (x-t)^{m-1}\, e^{2at}\, dt$$

$$\leqslant \frac{2ba^m\, e^{2ax}}{\Gamma(m)} \int_0^x (x-t)^{m-1}\, dt$$

$$= \frac{2b\,(ax)^m\, e^{2ax}}{\Gamma(m+1)}$$

since e^{2at} is an increasing function of t. The right side of (19) is independent of p and therefore for all values of p and all values of x in (0 T)

$$(20) \qquad \operatorname*{Lim}_{m \to \infty} {}_p\mathrm{R}_m = 0$$

which proves (8). We have yet to show that the functions $y_n(x)$ satisfy (1). This is equivalent to proving

$$(21) \qquad \operatorname*{Lim}_{m \to \infty} \int_0^x \mathrm{K}_n(x,t)\, \mathrm{F}_n(t\,;\, y_1^m, y_2^m \cdots)\, dt = \int_0^x \mathrm{K}_n(x,t)\, \mathrm{F}_n(t\,;\, y_1, \cdots)\, dt$$

This follows immediately on account of (20) or (8). In fact

$$\left[\int_0^x \mathrm{K}_n(x,t) \left\{ \mathrm{F}_n(t\,;\, y_4(t), y_1(t) \cdots) - \mathrm{F}_n[t\,;\, y_1^m(t), y_2^m(t) \cdots] \right\} dt \right]^2$$

$$\leqslant l_n^2 \int_0^x [\mathrm{K}_n(x,t)]^2\, dt \int_0^x \sum_{n:1}^{\infty} (y_n^m - y_n)^2\, dt$$

and the right side tends to zero as $m \to \infty$, for every n.

3. We shall now prove that the solution thus obtained is unique. Let us suppose that there exists another set of solutions $[z_n(x)]$ satisfying (1) identically, so that

$$(22) \qquad \sum_{n:1}^{\infty} (z_n)^2 < c$$

where c is a constant independent of x. Write

$$(23) \qquad \begin{cases} \mathrm{A}_m = \sum\limits_{n:1}^{\infty} (y_n^m - y_n)^2 \\ \mathrm{B}_m = \sum\limits_{n:1}^{\infty} (y_n^m - z_n)^2 \end{cases}$$

then

$$\sum_{n:1}^{\infty} (y_n - z_n)^2 \leqslant 2A_m + 2B_m. \tag{24}$$

As in (10) we will have

$$B_m \leqslant a \int_0^x B_{m-1}(t)\, dt \leqslant \frac{a^{m+1}}{\Gamma(m+1)} \int_0^x (x-t)^m B_0(t)\, dt \tag{25}$$

$$\leqslant \frac{ca^{m+1} x^{m+1}}{\Gamma(m+2)}$$

where $B_0(x) = \sum_{n:1}^{\infty} z_n^2 < c$, (25) shows that

$$\lim_{m \to \infty} B_m = 0. \quad \text{Also} \quad \lim_{m \to \infty} A_m = 0. \tag{26}$$

Hence from (24), letting $m \to \infty$ there

$$\sum_{n:1}^{\infty} (y_n - z_n)^2 \equiv 0 \tag{27}$$

This proves that $y_n \equiv z_n$, for every n.

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